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DTU Environment
Department of Environmental Engineering

PhD Thesis
September 2013

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Everything is vague to a degree, you do not realize till you have tried to make it precise.

Bertrand Russell

British author, mathematician, & philosopher (1872 - 1970)

Preface

This thesis comprises the research completed during a Ph.D. project carried out at the Technical University of Denmark, Department of Environmental Engineering from June 1st 2010 to July 23rd, 2013. Main supervisor for the Ph.D. Research was Associate Professor Rasmus Jakobsen and Professor Poul Bjerg was co-supervisor. The Ph.D. research program was funded by the Danish Council for Strategic Research under grant DSF-09-067234.

The thesis is organized in four parts: the first part explains the motivation behind the research and gives an overview of related current literature. The second part summarises the work conducted as part of the Ph.D. project outlining the main activities and findings. The third part provides a discussion on the work conducted putting findings into context before providing conclusions. The fourth part consists of the 4 papers and 3 technical reports which have resulted from the Ph.D. study listed below. These will be referred to in the text with the Roman numerals as papers I-IV and technical reports I-III.

Papers

I Cahill, A.G., Jakobsen, R., Mathiesen T.B., Jensen, C.K. Risks Attributable to Water Quality Changes in Shallow Potable Aquifers from Geological Carbon Sequestration Leakage into Sediments of Variable Carbonate Content. Accepted for publication. International Journal of Greenhouse Gas Control.

II Cahill, A.G., Jakobsen, R. Hydro-geochemical impact of CO_2 leakage from geological storage on shallow potable aquifers: A field scale pilot experiment. Int. J. Greenhouse Gas Control (2013), http://dx.doi.org/10.1016/j.ijggc.2013.03.015 -0.

III Cahill, A.G., Marker, P.A., Jakobsen, R. Hydrogeochemical and Mineralogical Effects of Sustained CO_2 Contamination in a Shallow Sandy Aquifer: A field scale controlled release experiment. Under review. Water Resource Research.

IV Cahill, A.G., Jakobsen, R. Geochemical Modelling of a Sustained Shallow Aquifer CO_2 Leakage Field Study. Submitted. Applied Geochemistry.

Technical Reports

I. Cahill, A.G., Jakobsen, R. Hydro-geochemical impact of CO_2 leakage from geological storage on shallow potable aquifers: Field Site Batch Experiment Investigation

II. Cahill, A.G., Jakobsen, R., Hjort-Larsen, C. Hydro-geochemical impact of CO_2 leakage from geological storage on shallow potable aquifers: A Laboratory Flow Tank Experiment

III. Cahill, A.G., Spangler, L., Dobeck, L., Thordsen, J., Jakobsen, R. Hydro-geochemical impact of CO_2 leakage from geological storage on shallow potable aquifers: ZERT field facility Core Study

Additional Information (Electronic Only)

Kevin Dome Storage Project: Overlying Formation Hydrogeological and Hydrogeochemical Technical Report. A.Cahill

In this online version of the thesis, the papers and technical reports are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from:

DTU Environment,
Technical University of Denmark,
Miljoevej, Building 113,
2800 Kgs. Lyngby,
Denmark,

reception@env.dtu.dk

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Enormous appreciation and thanks go first and foremost to my supervisor Rasmus Jakobsen, who has been a tremendous support and inspiration from start to finish. Without his incredible knowledge, wisdom, patience and efforts this project would not have been the success it has.

Equal appreciation is given for the hard work and expertise of Erik Lange, expert geo-technician. Erik's vast experience, attention to detail and skill made a very challenging applied field study possible. For his support and great company in the field (come rain, shine, wind or snow), I am eternally grateful.

I would like to thank the scientific staff at both DTU and GEUS for providing excellent analytical support during the project with particular thanks to Sinh Nguyen and Jørgen Kystol.

Thanks are further given to Dr. Lee Spangler and Dr. Laura Dobeck from the Energy Research Institute at Montana State University for hosting me during an extremely rewarding external research stay in Bozeman, Montana.

Massive appreciation is given to the enthusiastic and hard working students who assisted during the project including; Pernille Marker, Christian Hjørt Larsen, Tina Bay Mathiesen and Christian Kjær Jensen, without whom so much would not have been achieved.

Gratitude is extended to the excellent and professional administration staff at DTU environment, and in particular Anne Harsting, who made me feel more at home during my Danish adventure.

Hugs are given to all the people in DTU environment who have become my friends along this journey, of which there are too many to name. The people make the journey and the eclectic crew at this special department have made this 3 of the most enjoyable and exciting years of my life.

Love is given to my mother for her unconditional support for which I am always and forever indebted. And also to Shannon, for being there.

Abstract

Climate change induced by anthropogenic CO_2 emissions is widely accepted to be the greatest immediate threat faced by modern civilization. Carbon capture and geological storage (CCGS) is one of the most promising geo-engineering technologies currently within reach by which to, at least partially, mitigate this threat. The capture, compression and injection of CO_2 in supercritical state into deep saline aquifers is a technique which attracts criticism not least for its additional cost to energy production but more so for delaying transition to renewable energies and risks posed to the environment. Although considered highly unlikely following appropriate site selection, leakage of CO_2 from CCGS forms a major concern for both scientists and the public. Leakage would potentially occur through faults or abandoned boreholes and ultimately result in upward migration and discharge to the atmosphere. During migration CO_2 would dissolve into groundwater forming carbonic acid, induce water-rock reactions and thus change groundwater chemistry. Therefore prior to implementation of this potentially necessary technology, environmental risks associated with leakage must be understood.

Over the past 10 years scientists have worked in earnest to understand the potential effects of leakage in order that an informed decision on CCGS implementation can be made. This research can be broadly described as aiming to answer two key questions; how deleterious is leakage of CCGS to groundwater resources? and can it be detected geochemically?

Some common hydrochemical development is apparent from the literature however many aspects of hydrogeological and hydrogeochemical impact of leakage into shallow aquifers used in water supply remain unclear. In this Ph.D. study an integrated approach was employed in order to answer the two key questions regarding leakage of CO_2 into shallow aquifers. Consequently a combination of laboratory and field investigations were conducted supported by numerical geochemical modeling in order to identify, constrain and quantify processes controlling groundwater chemistry evolution. The output is 4 journal articles (1 in press and 3 submitted) and 3 technical reports.

In paper I and technical report I simple batch reactors were employed coupled to comprehensive sediment characterization to determine the likely effects of CO_2 on water chemistry in a range of shallow aquifers. Results showed aquifers can be broadly divided into three types; carbonate dominated,

silicate dominated and mixed. Each aquifer type showed distinct water chemistry evolution thus inherent risks vary. These studies also highlighted the complexity of risk assessment and detection caused by the range of formation types potentially overlying storage reservoirs.

Investigations described in Papers II, III and technical report II increase applicability to real leakage by observing in situ effects including groundwater flow. A silicate dominated shallow aquifer in Vrøgum, western Denmark forms the focus of study upon which a series of investigations were conducted. The main field study involved injection of 1600 kg of gas phase CO_2 into the shallow Vrøgum aquifer over 72 days with more than 770 water samples taken. In addition pre- and post-injection sediment cores were studied in order to assess sediment alteration and aid identification of controlling geochemical processes. Results show a significant lowering of pH and increase in electrical conductivity, but except for Al concentrations reaching up to 75 μmol/L, the detrimental effects on groundwater quality were limited. Groundwater chemistry evolves spatially and temporally during leakage, thus risks posed and the best methods for detection will also vary. In addition, 2 main phases of leakage were identified; a pulse phase of elevated ions moving with advective flow succeeded by increasing persistent acidification caused by buffering exhaustion (i.e. depletion of reactive minerals). Aqueous element concentrations were delineated into 4 generalized behaviors; 1. advective pulse (Ca, Mg, Na, Si, Ba and Sr,), 2. pH sensitive abundance dependent (Al and Zn), 3. complete removal (Mn and Fe) and 4. unaffected (K). Concentration behaviors were characterized by; 1. a maximal front moving with advective flow, 2. continual increase in close proximity to the injection horizon, 3. removal from solution to zero concentration and 4. no significant change.

Paper IV describes geochemical modeling conducted in support of field and laboratory activities and proposes that gibbsite derived Al^{3+} driven cation exchange can explain the majority of the water chemistry evolution at Vrøgum. In addition buffering exhaustion/sediment depletion is corroborated explaining increasing acidification observed. Results infer risks associated with and how best to detect leakage will change with time and also increase with depth. Consequently water quality may become more deleterious as a leak matures and will vary with depth.

Resume

Der er bred enighed om at klimaforandringer forårsaget af menneskeskabte CO_2 udledninger er den mest umiddelbart forestående trussel for den moderne civilisation. Separation af CO_2 og lagring i undergrunden også kaldet CCGS [Carbon Capture and Geological Storage (CCGS) er en af de mest lovende teknologier til, i hvert fald delvist, at afværge denne trussel og det er en teknologi der er indenfor rækkevidde. Separationen, kompressionen og injektionen af superkritisk CO_2 i dybe salte grundvandsmagasiner er en teknik der er blevet kritiseret, ikke mindst på grund af den medfølgende forøgelse af energiforbruget, men i høj grad også fordi det vil udsætte overgangen til bæredygtige energiformer og medføre miljørisisci. Selvom det anses for meget usandsynligt, under forudsætning af omhyggelig udvælgelse af velegnede steder til underjordisk lagring, er lækage af CO_2 fra CCGS en betydelig bekymring for såvel forskere og befolkningen. Lækagen ville kunne ske langs forkastninger eller efterladte boringer og ville i sidste ende resultere i en opadgående migration og en frigivelse til atmosfæren. Under migrationen ville CO_2 opløses i grundvandet og danne kulsyre, forårsage vekselvirkninger mellem vandet og materialerne i grundvandssystemet og dermed ændre grundvandskemien. Derfor er det vigtigt at vi, forud for en implementering af denne potentielt nødvendige teknologi, har en forståelse af de miljømæssige konsekvenserer relateret til en lækage.

I løbet af de sidste 10 år er der blevet forsket ihærdigt i at forstå de potentielle effekter af en lækage for at sikre at en velunderbygget beslutning om en eventuel implementering af CCGS. Forskningen kan overordnet siges at forsøge at besvare to centrale spørgsmål: Hvor skadeligt er et udslip for grundvandsressourcen? Og, hvordan kan det detekteres geokemisk? Undersøgelserne peger på nogle fælles forventede udviklinger i grundvandskemien, men mange af de hydrogeologiske og grundvandskemiske effekter som vil forårsages af en lækage der når et grundvandsmagasin med drikkevandskvalitet er stadig uklare.

I dette ph.d. studie er der anvendt en integreret tilgang for besvare de to centrale spørgsmål relateret til lækage af CO_2 ind i grundvandsmagasiner. Det indebærer at der er gennemført en kombination af laboratorie og feltundersøgelser understøttet af af numerisk modellering for at indentificere afgrænse og kvantificere de processer der kontrollerer grundvandskemiens udvikling. Udkommet er 4 tidsskrifsartikler (1 publiceret og 3 der er indsendt til tidskrifter) og 3 tekniske rapporter.

I artikel I og teknisk rapport I er der brugt simple flaskeforsøg i kombination med detaljeret sediment karakterisering for at beskrive det sandsynlige effekter CO_2 på grundvandskemien i en række typiske grundvandsmagasiner. Resultaterne viser at grundvandsmagasiner groft kan inddeles i tre typer, silikat dominerede, karbonat dominerede og blandede. Hver af magasin typerne viste en karakteristisk udvikling i grundvandskemien, som indebærer at de tilknyttede risisci vil variere. Disse studier peger på komplexiteten i risikovurderingen og detektionen da der over et givent CO2 lager kan ligge mange forskellige grundvandsbærende bjergarter.

Undersøgelserne beskrevet i artikel II, III og teknisk rapport II kommer tættere på forholdene ved en virkelig lækage idet der ses på in situ effekter i et grundvandssystem med strømning. Et terrænnært grundvandsmagasin domineret af silikat mineraler er udgangspunktet for et forsøg med en sandfyldt strømrende, efterfulgt af et pilot og et længerevarende hovedforsøg med injektion a CO_2 i grundvandsmagasinet. Hovedfeltforsøget indebar injektion af 1600 kg CO_2 gas i Vrøgum magasinet i løbet af 72 dage samt udtagning af 770 vandprøver. Derudover blev der udtaget sedimentkerner før og efter injektionen for at se på ændringer i sedimentet og understøtte identifikationen af de styrende geokemiske processer. Resultaterne viser en betydelig sænkning af pH og stigning i den elektriske ledningsevne, men bortset fra Al koncentrationer der nåede 75 µmol/L var forringelsen af grundvandets kvalitet meget begrænset. Grundvandskemien vil udvikle sig i både tid og rum under en lækage og derfor vil risisci og de mest egnede metoder til at detektere en lækage også variere. Der blev observeret to hoved faser knyttet til en lækage, en puls hvor forhøjede koncentrationer af ioner bevægede sig med grundvandsstrømmen efterfulgt af en tiltagende forsuring når bufferkapaciteten opbruges, pga. opløsning af de reaktive mineraler. Opløste stoffer udviste 4 mønstre; 1. en puls i form af en front med maximal koncentration der bevægede sig med grundvandet (Ca, Mg, Na, Si, Ba og Sr), 2. en fortsat forøgelse af koncentrationen tæt på injektionen af pH følsomme stoffer (Al and Zn), 3. en komplet fjernelse til koncentrationer nær nul (Mn and Fe) og 4. ingen koncentrationsændringer af betydning (K).

Artikel IV beskriver den geokemiske modellering some gennemført for at understøtte felt og laboratorie aktiviteterne og som når frem til at den centrale spiller er Al fra gibbsite opløsning som igen forårsager ionbytning i system og giver ophav til den grundvandsgeokemiske udvikling i Vrøgum magasinet. Modellen peger på en udtømning af det reactive gibbsite reservoir og dermed bufferkapaciteten som forklaring på den tiltagende observerede forsuring.

Resultaterne peger på risisci forbundet med lækage og at den bedste måde at detektere en lækage vil ændre sig med tiden og tiltage med dybden. Konsekvensen er at skaderne på grundvandet vil forværres som en lækage modnes og vil variere med dybden.

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Abbreviations

CCGS	Carbon Capture and Geological Storage
DO	Dissolved Oxygen
EC	Electrical Conductivity
IPCC	Intergovernmental Panel on Climate Change
MMV	Monitoring, Measurement and Verification Program
P_{CO2}	Partial Pressure of CO_2
SI	Saturation Index
TIC	Total Inorganic Carbon
USDW	Underground Supply of Drinking Water

1 Thesis structure

The thesis begins by providing a general overview of CO_2 induced anthropogenic climate change and outlines the concept of geological storage as a mitigation method. The main risks posed by this geo-engineering technology (specifically leakage of CO_2 into shallow groundwater resources) are then described followed by a brief overview of associated key chemistry concepts. Next a comprehensive review of the current literature is made and knowledge gaps identified. The objectives of the thesis are then stated before an overview of the work conducted, including results, is given. First a brief overview of the field site on which most work has focused is provided followed by descriptions of associated laboratory, field and modelling work. Work conducted is summarized in the thesis but not described in detail. The work completed is described in detail at the end of the thesis, as either a published/submitted journal article or a technical report. The description of activities and results is followed by a discussion exploring the implications of attained results. Finally, recommendations for future research are made before the 4 papers and 3 technical reports which have resulted from the Ph.D. study are presented in their entirety. The technical reports give a brief overview of experimental work conducted during the Ph.D. and present selected results only. Technical reports have been formed where results of value and significance to this field of research have been attained; however there was insufficient time or detail with which to publish. Thus technical reports are not implied to be of publishable quality.

2 Introduction

2.1 Background

Carbon dioxide (CO_2) is a simple molecule comprised of 2 oxygen atoms covalently double bonded to a carbon. CO_2 forms a crucial constituent of the global carbon cycle on which life on earth ultimately depends [1]. As a greenhouse gas, atmospheric CO_2 acts to regulate global temperature, fortuitously maintaining a range conducive to life [2]. Atmospheric concentrations naturally fluctuate over geological time and have been attributed to climate change during the Earth's history [3]. Fossil fuels (coal, oil and natural gas) currently provide 87% of the world's energy needs [4] and their primary combustion product is CO_2. Upon combustion, fossil fuel derived CO_2 is usually emitted to the atmosphere, a practice in operation since the industrial revolution. This prolonged, persistent and global scale emission must ultimately change atmospheric composition [5]. Since the industrial revolution atmospheric CO_2 levels have been consistently increasing [6]. This phenomenon has been recognized and accepted by the vast majority of the scientific community as directly attributed to fossil fuel combustion and anthropogenic emissions [7-9]. Proven reserves of fossil fuels, even at their most conservative, can provide energy for the next century at least. In addition recent technological advances (i.e. directional drilling and hydraulic fracturing methods) have further increased the scope of natural gas abstraction from previously unusable shale deposits [10]. The relative abundance and low cost of fossil fuels combined with challenges in transferring to renewable energy sources mean continued use (and CO_2 emission) is certain for the foreseeable future.

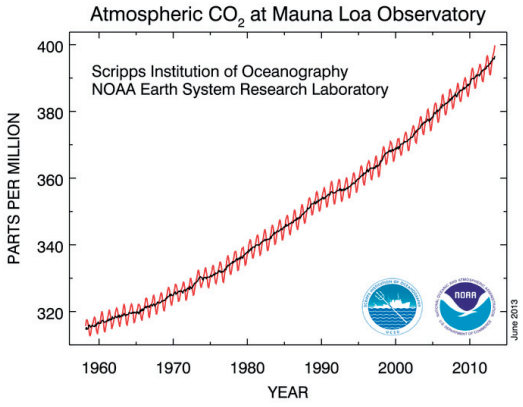

Figure 1. Atmospheric CO_2 concentrations measured at Mauna Loa, Hawaii taken from National Oceanic and Atmospheric Administration home page [11].

In May 2013 atmospheric CO_2 levels surpassed 400 ppm for the first time in 4.5 million years [11]. This milestone signifies mankind's movement into unchartered territory regarding the earth's climate. The effect of elevated atmospheric CO_2 is unequivocal warming in the earth's average temperature [12]. Predictions vary dependent on projection model and future emissions scenario employed however an increase of 1.1 – 6.4 degrees centigrade in earths average temperature by the end of the 21st century is accepted [13]. This average increase will result in enormous change to the earth's climate. Sea level rise, increased frequency of extreme weather events (e.g. drought and flooding) and ocean acidification are accepted consequences [14-18]. In turn these processes will have unprecedented implications for society and social systems [19]. Habitat inundation and food supply disruption are the main issues from which it is estimated hundreds of millions of people will be affected [20-22]. Consequently climate change, and more specifically anthropogenic global warming, is arguably the biggest threat to modern civilization faced by mankind.

Based on the findings of extensive research the Intergovernmental Panel on Climate Change (IPCC) demand immediate and ongoing mitigation measures to be implemented in order to slow and limit the effects of global warming [23]. As such many different policies have been employed in order to slow the rate of emissions and adapt modern society to handle a changing climate [24-25]. In addition various technologies to further mitigate global warming have been suggested as requirements for stabilization of atmospheric CO_2 concentrations. One of the key technologies described as potentially necessary in this adaptation is carbon capture and geological storage [26].

2.2 Carbon capture and geological storage

Carbon capture and geological storage (CCGS) involves capture of gas phase CO_2 from point sources (e.g. power stations, cement factories and industrial plants), compression to a supercritical state and injection into deep geological storage reservoirs [27-28]. This geo-engineering technology is in some ways the reverse of fossil fuel exploitation, allowing combustion whilst preventing atmospheric release. Conventional oil and gas reservoirs are formed when geological conditions permit trapping of the resource via a cap rock for geological time scales. CCGS exploits this phenomenon by injecting supercritical CO_2 into similarly suitable storage reservoirs (Figure 2). The concept was first developed based on enhanced oil recovery techniques [29]

and as a method to avoid carbon tax [30]. Its use as a standalone global warming mitigation technique has since been pursued. Consequently it now forms one of the most promising methods currently considered to allow continued use of fossil fuels whilst mitigating climate change. Implementation of the technique on a scale likely to mitigate climate change however faces many challenges including; economics, ethics, logistics and public acceptance [31-32]. The technology is complex involving interdisciplinary input from many fields. For a general overview of CCGS the reader is referred to one of the many pieces of literature on the technology, e.g. [26-27, 33-37]. A key principle of the technique is that significant amounts of CO_2 should not leave the storage reservoir over any timescale, i.e. leakage should not occur. However, the consequences of leakage must still be fully understood in order that an informed decision on deployment of CCGS on a global scale can be made.

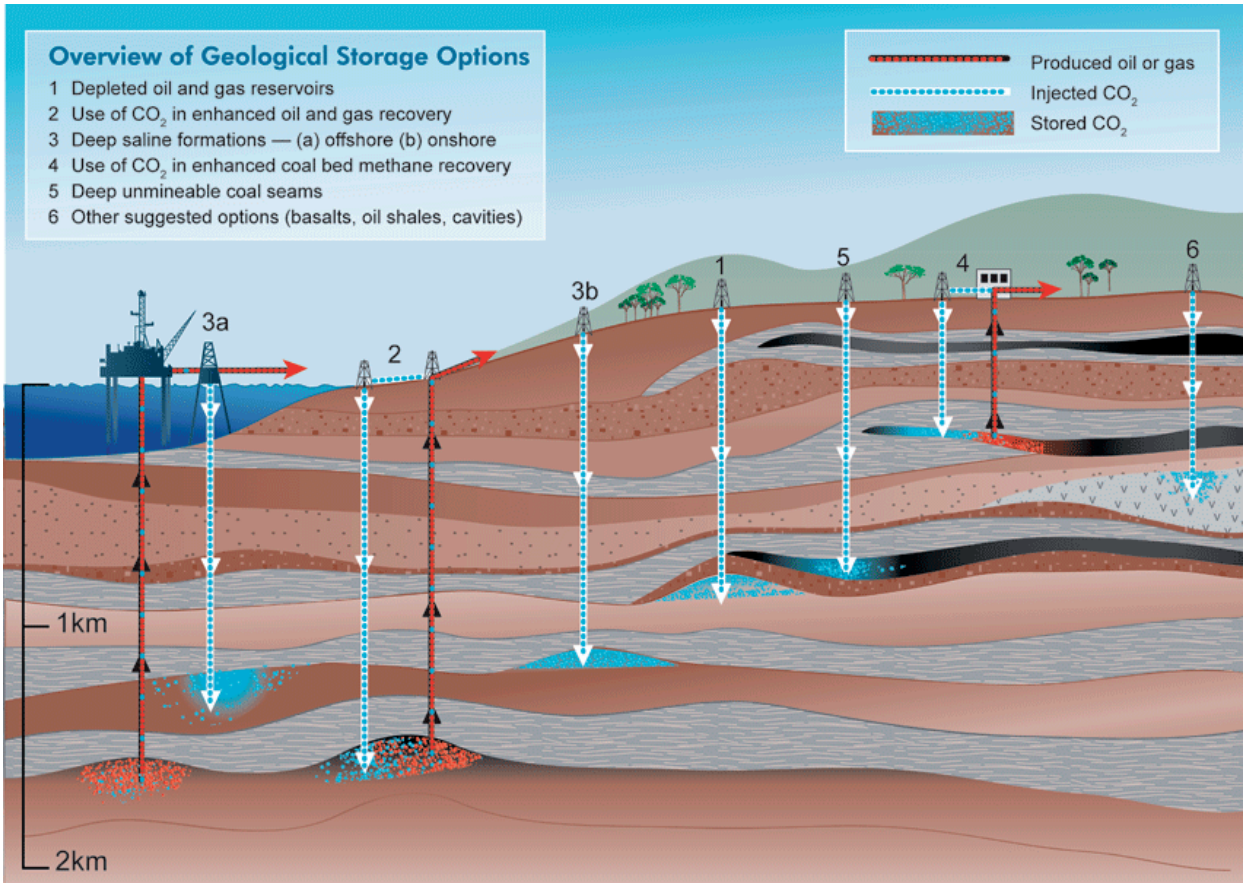

Figure 2. Potential geological storage methods and target reservoirs. Taken from the IPCC Special Report: Carbon Dioxide Capture and Storage [38].

2.3 Environmental risks of CCGS

The main environmental risks associated with CCGS can be broadly considered as; displacement of reservoir brine which is forced from the pore space during storage, and leakage of injected CO_2 itself. The mechanism of leakage for both brine and supercritical CO_2 is most likely via abandoned wells or faults in the cap rock [39]. During CO_2 injection large pressure gradients are created and subsequently propagated large distances. This pressure propagation could induce migration of reservoir brine through distant abandoned wells/fault zones into overlying potable groundwater [40-42]. Reservoir brines are of extremely low quality and would undoubtedly render fresh groundwater unusable [43]. Brine displacement is however not the focus of the current study and will not be considered further. For more information the reader is directed to the excellent publications available in the literature previously cited. Following careful site selection, leakage of CO_2 itself is considered highly unlikely. Nonetheless, knowledge on the effects of leakage is essential in order to implement the technique safely on a global scale and gain public acceptance. Should leakage occur, supercritical CO_2 from the storage reservoir would migrate through abandoned wells or faults and be driven towards the surface by buoyancy. At pressures above 800 m depth supercritical CO_2 will convert to a gas phase. Gas phase CO_2 would dissolve into the groundwater whilst continuing to rise via buoyancy forces ultimately reaching the surface (Figure 3).

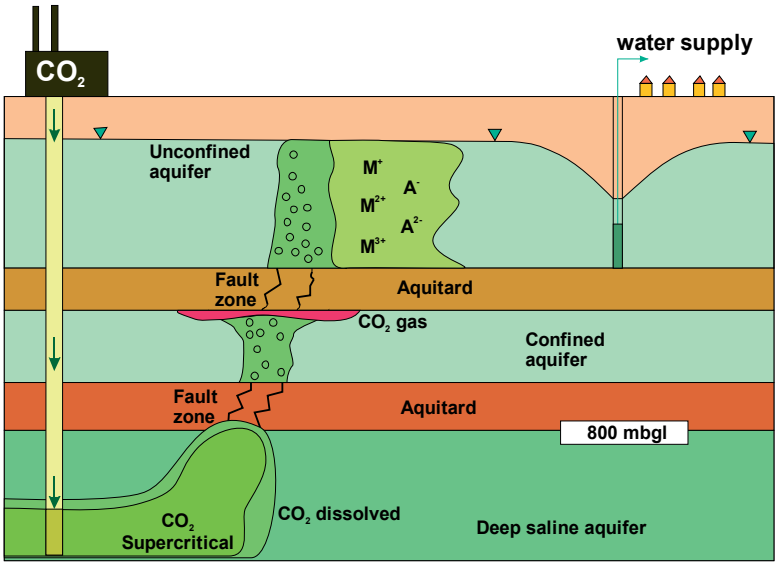

Figure 3. Cross section of typical sedimentary basin exploited for carbon capture and geological storage showing leakage concept including dissolved plume of CO_2 in the shallow potable aquifer.

Aside from issues of efficiency and liability, leakage of CO_2 and migration into shallow potable aquifers is a major cause for concern among scientists, regulators and indeed the public. It poses two key questions which must be addressed before the technology can be implemented;

- What are the risks posed by leakage of CO_2 from CCGS to shallow groundwater resources and the environment? and;
- Can a leak be detected in shallow groundwater and if so how?

These are the questions which will form the focus of this Ph.D. thesis which looks to address the issue of leakage of CO_2 into shallow potable aquifer systems.

2.4 The carbonic acid system

Shallow groundwater is a major supply of potable water throughout the world and is inherently found overlaying potential CCGS reservoirs. As such this valuable resource would be at risk from CO_2 leakage thus this issue has become an area of intense research in the last 5 – 8 years. Concerns regarding groundwater resources and human health centre on the properties of dissolved CO_2 gas which forms carbonic acid. Once in aqueous form, CO_2 associates with a water molecule to form carbonic acid which subsequently dissociates, releasing protons and a carbonate anion (based on approximate equilibrium constants under standard conditions):

$$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)}$$

$$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_2^* \qquad (K_H = 10^{-1.5})$$

$$H_2CO_2^* \rightleftharpoons HCO_3^- + H^+ \qquad (K_2 = 10^{-6.3})$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad (K_3 = 10^{-10.3})$$

This dissociation decreases pH and feeds into the carbonate system [44]. The amount of CO_2 in aqueous form depends on partial pressure of CO_2 (P_{CO2}), i.e. Dalton's Law [45]. Greater P_{CO2} induces greater dissolution of gas phase CO_2, formation of carbonic acid and dissociation (i.e. proton release). Under normal conditions atmospheric CO_2 will naturally dissolve into water forming dilute carbonic acid based on atmospheric P_{CO2} (approximately $10^{-3.5}$ atm).

In shallow aquifers this can be higher depending on depth and conditions, e.g. 10^{-3} – 10^{-2} atm [44]. During leakage P_{CO2} in a shallow aquifer could be 10^{0} – $10^{2.5}$ atm depending on depth, thus acidification could be significant. The influence of dissolved CO_2 on pH and the carbonate system results in significant control being exerted on water chemistry and water-rock interactions in shallow potable aquifer systems. Many key geochemical processes which determine water quality involve and/or are affected by protons.

2.5 Geochemical processes

Aqueous speciation, mineral dissolution/precipitation, ion exchange and surface complexation are all key geochemical processes which control water chemistry. These phenomena are ultimately influenced by pH and therefore indirectly by P_{CO2}. Introduction of CO_2 into a shallow aquifer will change the carbonic acid system equilibria and have immediate effect on linked geochemical processes, as conceptualized in Figure 4. For an overview of these geochemical processes including governing equations and their derivation the reader is referred to any basic hydro-geochemistry text book (e.g. [44]).

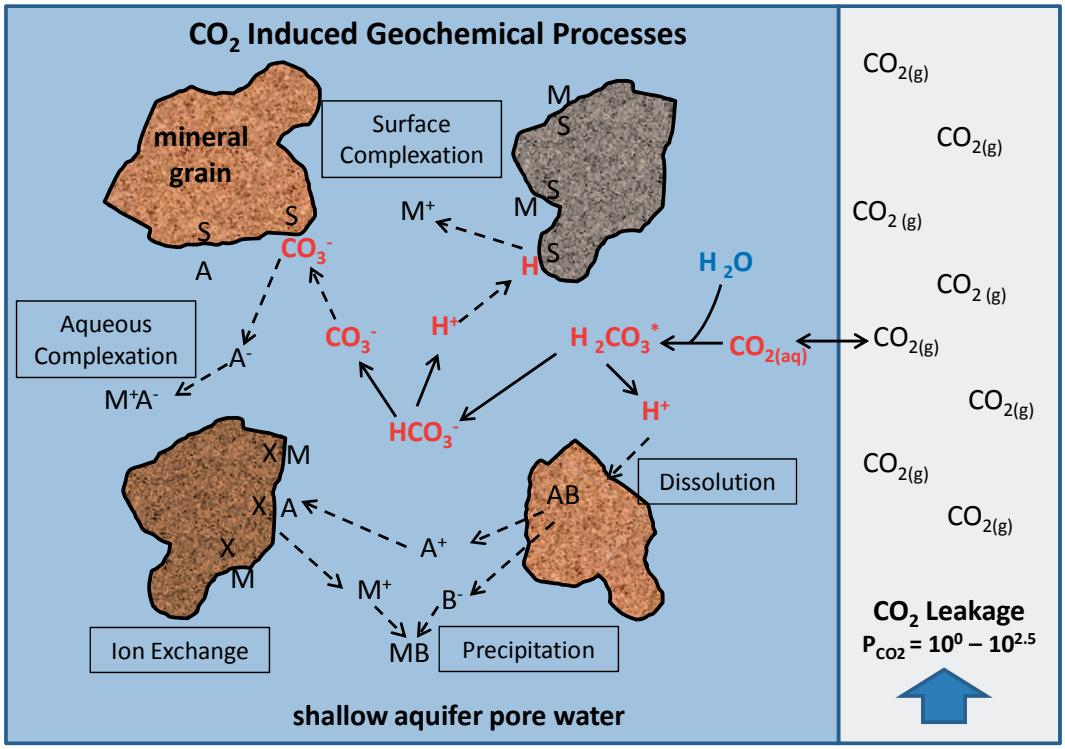

Figure 4. Schematic showing generalized geochemical processes involved in or induced by dissolution of CO_2 in a shallow aquifer system: aqueous complexation, mineral dissolution, precipitation, ion exchange, surface complexation.

3 Environmental assessment of CO_2 contamination in shallow aquifers

In order to assess the hydro-geochemical changes induced by leakage of CO_2 into shallow potable aquifers, scientists have employed three main methods. These can be broadly defined as; laboratory studies, field studies and numerical modelling studies. The current state of the art for each will be described in the proceeding sections.

3.1 Laboratory studies

Laboratory studies allow CO_2 induced geochemical change to be directly measured in a controlled setting. Laboratory studies limit the challenges associated with field studies, i.e. heterogeneity, continuity, uncertainty and logistics and are arguably more applicable than generic modelling studies. In spite of their convenient nature, relatively few have been reported in the literature, those which have are limited to simple batch reactor style studies. For example Lu et al. explored the effects of CO_2 contamination on U.S. gulf coast region sediments [46]. In this study sediment mineralogy was first determined by XRD and SEM EDS. Subsequently disaggregated rock samples (95 g) were mixed with NaCl supplemented de-ionized water (500 ml) in closed Erlenmeyer flasks. Initially reactors were injected with argon before 2 weeks of CO_2 injection with water chemistry monitored. The injection regime delivered gas 1 in every 20 minutes during both injection phases and water samples were taken throughout with aqueous element concentrations determined by ICP–MS. Results were interpreted as showing two types of cation behaviours. Type 1 cations (Ca, Mg, Si, K, Sr, Mn, Ba, Co, B and Zn) rapidly increased then stabilized. Type 2 (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) initially increased but then declined below background levels. The majority of chemistry change was attributed to calcite and dolomite dissolution with carbonates in general inferred as the largest risk to water quality. Strong negative correlation of pH to cation release rate was observed and type 2 cation increases were inferred to be self limiting due to adsorption processes. Overall carbonate based cations were suggested as the most suitable geochemical markers for leakage detection and reactors were said to present a worst case scenario due to the high gas:water/rock ratio utilized.

Another similar study was performed by Little and Jackson however over a much longer time period [47]. In this study sediments from the U.S. obtained from Aquia and Virginia beach, Mahomet and Ogalalla aquifers (400 g aliquots) were mixed in bottles with nano-pure water in a ratio of 3:1 (water:rock). A constant stream of CO_2 was injected into each reactor for up to 344 days with concurrent monitoring of water chemistry evolution.

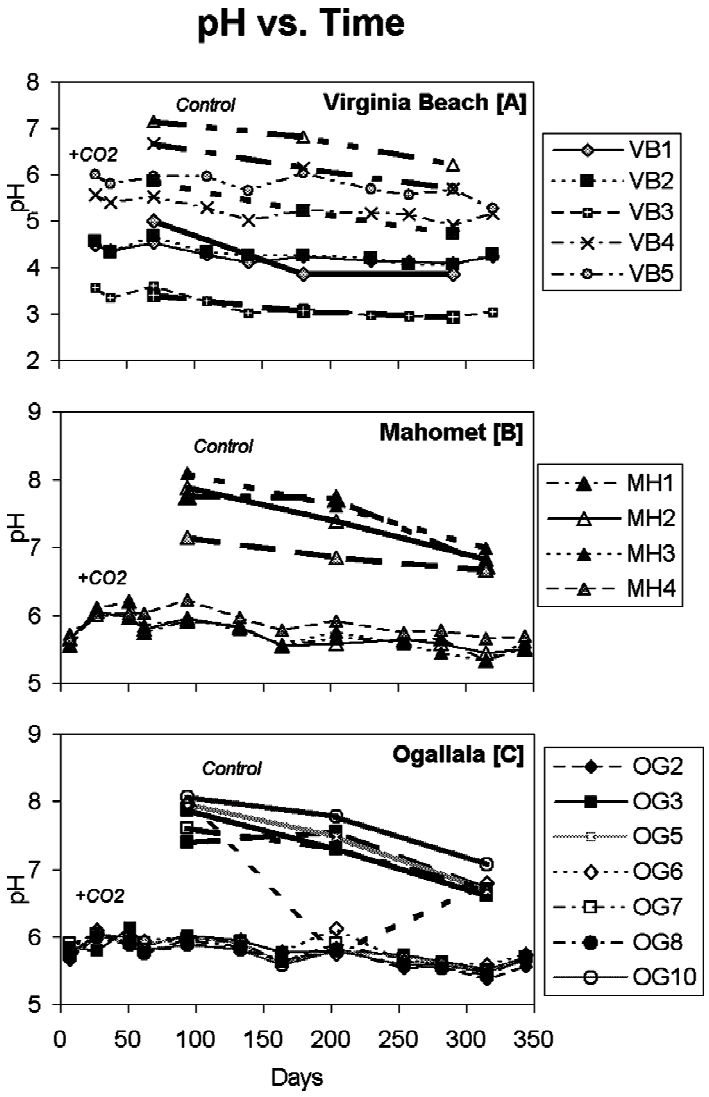

Figure 5. pH in groundwater experiments plotted against time. +CO2 experiment data collection began on day ~10. Control experiment data collection began on day ~45.

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Results showed pH decreases of 1 – 2 units (Figure 5) and significant increases in Li, Mg, Ca, Rb, Sr, Mn, Fe, Co, Ni, and Zn for most sediments peaking after 2 weeks. Elements Al, Mn, Fe, Zn, Cd, Se, Ba, Tl, and U were

seen to approach or exceed guideline drinking water values whilst Li, Co, U, and Ba were still increasing after 300 days. Some elements, i.e. Ca, Sr, Mn, and Ba, were seen to fluctuate over the experimental period. Results confirm the importance of studying significant temporal scales with relatively high frequency in order to assess risks adequately as continued increases and fluctuation would have not been identified by a study period of less than 50 days. It was suggested that metal availability should be a key selection criteria for locating a CO_2 storage reservoir. Also lack of buffering capacity was identified as inferring greater risk for mobilizing pH sensitive metals in greater quantities. Detection of leakage was suggested via dissolved inorganic carbon, alkalinity, pH, Mn, Fe and Ca as these parameters showed significant and consistent change across all sediments investigated.

3.2 Field and integrated studies

Field studies involve measuring water chemistry in shallow potable aquifers following some form of artificial or natural CO_2 elevation. They vary in methodology and can be broadly categorized as either leak simulations (gas phase CO_2 or CO_2 equilibrated water injection) or natural analogue studies. These investigations form arguably the most applicable method as they directly observe in situ effects which would likely take place during leakage.

The ZERT field facility was the first of its kind for assessing various CO_2 surface detection methods [48]. This bespoke facility has been operated since 2007 and comprises a 100 m long horizontal pipeline at 2 m depth divided into 6 CO_2 injection zones. Mass flow for each zone is discreet (i.e. controlled by a packer system) allowing CO_2 to be injected at varying rates and durations for detection equipment testing. One section (zone 6) was used for a comprehensive groundwater study during the 2008 field season whereby 300 kg/day of CO_2 was injected through the whole pipe length over 29 days [49]. A total of 80 water samples (measured for physico chemistry and aqueous ion concentrations by ICP MS) were taken from a network of 5 well pairs (1.5 m and 3 m depth), 2 m up and 6 m down gradient of the injection screen (Figure 6). Results showed immediate pH decrease (approximately 1.4 units), alkalinity and EC increase (+900mg/l and +1200 μS/cm respectively) and concurrent increases in aqueous ion concentrations. Elements identified as increasing significantly and thus potentially suitable parameters for leak detection were Ca, Mg, Fe and Mn. Buffering by carbonate minerals and desorption/ion exchange were identified as the most likely causes of water

chemistry change, however these processes were not quantified. Dissolved elements showed significant fluctuation during the experimental period which was attributed to recharge caused by precipitation. This study was unique and for several years no other studies focusing on groundwater chemistry were published.

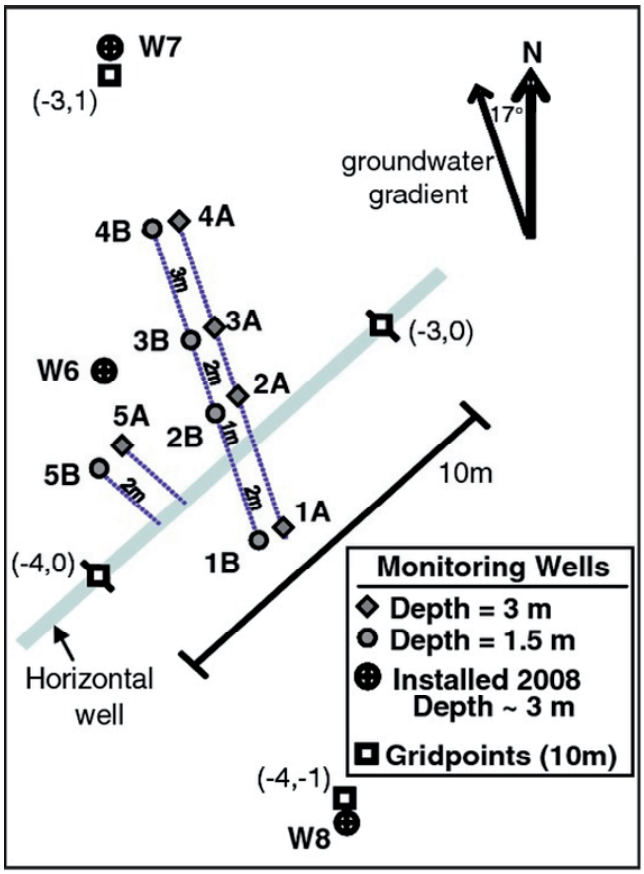

Figure 6. Location of water-monitoring wells in relation to the surface trace of the slotted horizontal pipe in zone VI of the ZERT site

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Fortunately this changed when results from several new field studies recently became available in 2012 and 2013. One of these was an experiment by Peter et al. conducted in Brandenburg, Germany. This experiment involved injection of 787 kg of gas phase CO_2 into a confined silicate aquifer at 18 m depth [50]. The injection lasted 11 days with subsequent monitoring of the dissolved phase plume conducted over 6 months and approximately 50 m of flow. Currently an isotope fractionation study has been published [51] in addition to an overview of the experiment's design and implementation includ-

ing preliminary results [50]. Results are currently reported for only one sample point 5m down flow of injection and show CO_2 induced water chemistry changes manifest as 150 μS/cm increase in electrical conductivity, concurrent increases in aqueous ions coupled to a decrease of 1 pH unit. No dissolved elements exceeded maximum drinking water limits at any time during the experiment for this observation point at least. A further publication to show more data from 669 groundwater samples taken from the 34 monitoring wells over the experiments duration is in progress and should show more detail of the simulated leaks development, temporally and spatially. Another recent study by Yang et al. studied the geochemical changes occurring during a push-pull test with CO_2 equilibrated water in a siliclastic aquifer [52]. Groundwater from the Cranfield shallow aquifer was abstracted, equilibrated with 1 bar CO_2 and infused with NaBr tracer before reinjection of 3.82 m^3 at 55 – 73 m depth over 10 hours. After 55 hours 15.14 m^3 of ground water were abstracted from the well and differences between initial and final chemistry determined including; physico-chemistry, dissolved inorganic carbon and aqueous ion concentrations. Clear enrichment of major and minor cations was evident, particularly Ca, Mg, K and Si, which was attributed to silicate and carbonate dissolution. Trace element enrichment was also observed and attributed to dissolution and desorption although no direct evidence for either processes were provided with carbonate not actually detected in the sediment. A numerical mixing model was also utilized to assess chemistry changes with deviation attributed to CO_2 induced geochemical processes. Consequently clear deviation was observed supporting CO_2 induced changes in chemistry composition had occurred. No elements were seen to exceed their safe drinking water limit during the study and pH, DIC, $\delta^{13}C$ of DIC were suggested as geochemical indicators of leakage.

Another field method to assess the potential effects of CO_2 contamination in shallow aquifers is to study natural analogues of leakage. There are many studies regarding natural CO_2 discharge at geologically active areas, e.g. Mammoth Mountain, California [53-54] and Mt. Vesuvius, Italy [55], however they usually lack direct application to a CCGS context. However, one natural analogue study conducted by Keating et al. does transfer field observations directly to the context of CCGS leakage [56]. In this study a shallow sandstone aquifer known to be CO_2 contaminated in Chimayo, New Mexico was studied. The Chimayo aquifer exhibits discharge of CO_2 at the surface (i.e. CO_2 geysers) in conjunction with high levels of dissolved CO_2 in the groundwater (Figure 7). Samples from wells and springs were taken and their

composition studied in conjunction with basic geochemical modelling with PHREEQC. This allowed the control of groundwater chemistry to be attributed to carbonate dissolution caused by high P_{CO2}. Inflow of brackish, high P_{CO2} fluid from underlying strata was also identified. Elevated P_{CO2} was seen to induce buffering by carbonate minerals thus pH reductions were minimal and in situ mobilization of trace metals limited. The greatest detriment to water chemistry was attributed to brackish water inflow as this fluid also contained many hazardous trace elements. This study exploited a natural occurrence of CO_2 contamination allowing extremely useful observations to be made however their applicability is somewhat limited. Systems such as Chimayo are generally mature with CO_2 having influenced chemistry of these systems for geologic timescales prior to study. As such early temporal evolution is missed which, as this thesis will show, is key to understanding leakage.

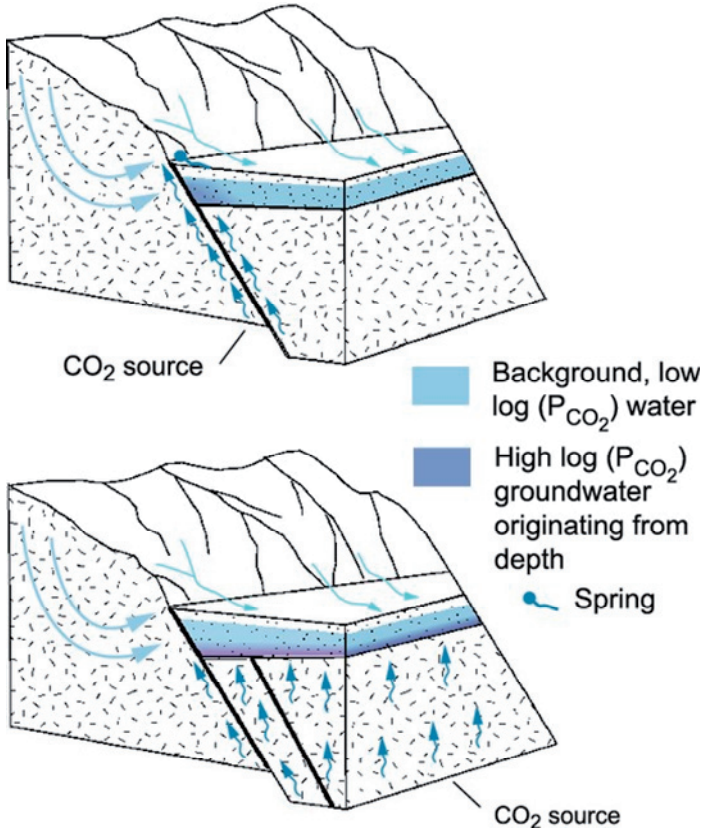

Figure 7. Two types of natural analogs (a) CO_2 rises with deep water along a fault and forms a CO_2-rich spring, b CO_2 rises with deep water along a faults and diffuses into shallow aquifer water. CO_2 degasses at springs and also along the water table to the vadose zone.

The most powerful of field studies are those which take an integrated approach. Trautz et al. for example conducted a leakage simulation in a confined, anoxic, silicate aquifer in Escatawpa, Mississippi [57]. In this study a high level of laboratory characterization was employed in conjunction with reactive transport modelling to interpret results and identify controlling geochemical processes. The study formation comprised a fine grained, silty sand aquifer with minor clays present at 47 to 55 m depth. A dipole system was employed whereby abstracted groundwater was equilibrated with gas phase CO_2 at in situ conditions (i.e. pressure) before reinjection (Figure 8). Following a background period using argon tracer, the CO_2 charged dipole system was subsequently operated over 5 months with groundwater samples taken from a network of 4 monitoring wells over a flow distance of 63 m. Results for MW 3 (5 m down flow) show a distinct "pulse" effect whereby certain elemental concentrations, EC and alkalinity were observed to peak relatively fast (i.e. after 24 days) before decreasing to slightly above background levels. This pulse behaviour is evident even though continuous injection of CO_2 charged groundwater is maintained. Concurrently pH was observed to decrease and remain depressed consistently throughout, the first time such phenomena have been identified. A model of the experiment was developed using TOUGHREACT V2 [58] which included various geochemical processes based on measured laboratory results. Dissolution/precipitation, cation exchange and surface complexation processes were included. Subsequently the model was able to simulate the pulse effect including physico chemistry and elemental concentrations relatively well. The study concluded that water chemistry changes were likely a result of rapid ion exchange/desorption processes coupled to dissolution of small amounts of finite reactive minerals. These rapid processes generated the observed pulse like effect and were likely followed by slower dissolution processes. The evolution of chemistry observed has significant and profound implications for leak detection and risks to water resources. This study highlights the importance of employing significant temporal and spatial scales, the inclusion of flow and support from laboratory testing and geochemical modelling in order to understand and interpret results.

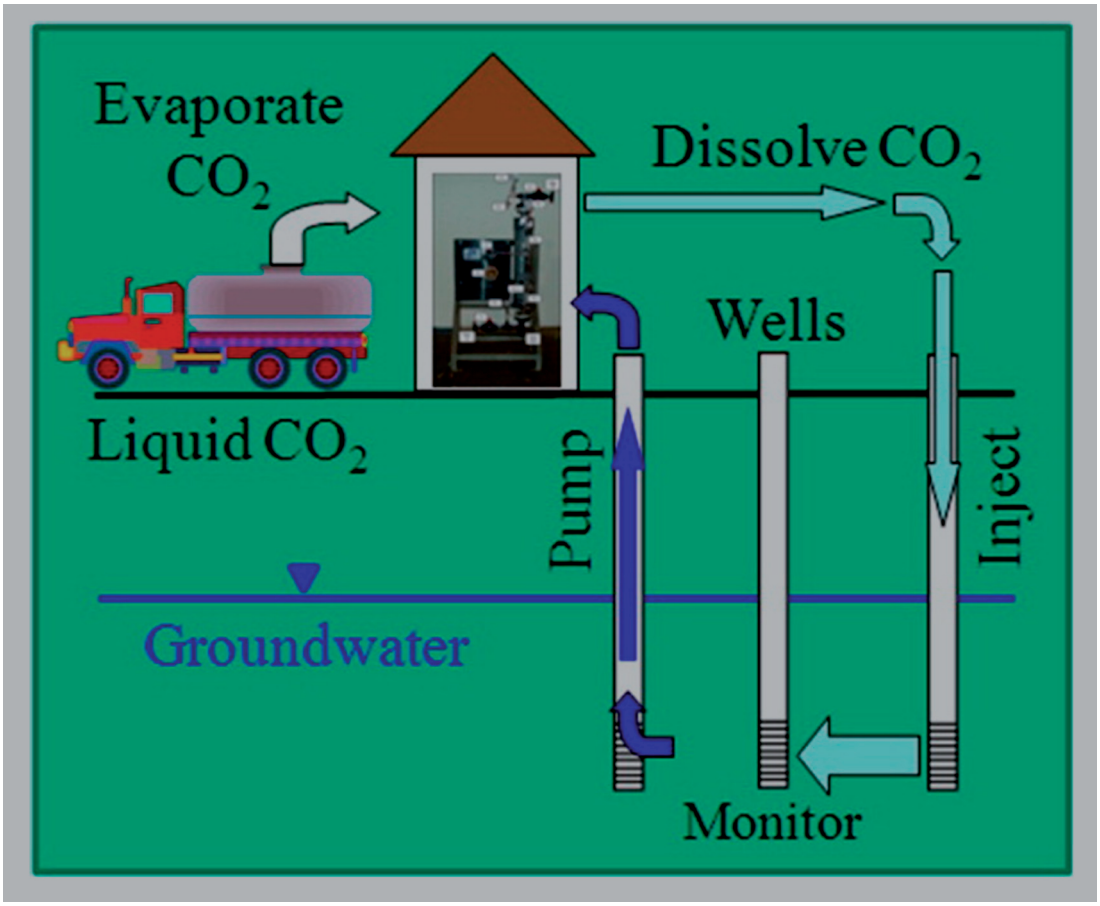

Figure 8. CO_2 charged groundwater dipole experiment as employed by Trautz et al.

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In spite of the excellent field work conducted over the last few years more is required. The full range of conditions potentially affected by leakage have not been considered. This can be seen by comparing the leakage simulation field studies described previously which are summarized in table 1. From this table it is clear that settings and methods used vary considerably, particularly spatial and temporal scales. How a leak will actually manifest in reality is not clear or agreed upon, however most likely it would be significant spatially and temporally (reflected in the last row).

Table 1. Overview of physical leakage simulations currently reported in the literature including key methodology components in comparison to how a leak would likely manifest.

Study	Experiment Type	Leakage/Injection period (days)	Leakage Rate (kg/day CO_2)	Temporal scale (days)	Spatial Scale (m)	Aquifer Type	Depth (m)
ZERT	gas phase injection	28	300	28	6	phreatic carbonaceous sand and gravel with significant clay	1.5
Brandenburg	gas phase injection	11	71.5	180	50	confined silicate	18
Escatawpa	CO_2 charged groundwater dipole	150	saturated at formation pressure	365	63	confined anoxic silicate with some clay	47 - 55
Cranfield	CO_2 charged push pull	3	saturated at 1 bar pressure	4	N/A	confined silicate with some clay minerals	55 -73
REAL LEAK	**gas phase CO_2 or CO_2 charged groundwater infiltration from deep subsurface**	**years to decades**	**1 - 10^6**	**decades to centuries**	**100's to 1000's**	**All possible sedimentary formations**	**0 - 300**

3.3 Geochemical modelling

Geochemical modelling involves the use of computer codes to describe changes in chemistry likely to occur following leakage based on accepted mathematical descriptions. Numerical models can be 1, 2 or 3 dimensional and allow inclusion of various geochemical mechanisms and physical processes such as surface complexation and multi or single phase flow. Numerical models are either generic, include some measured parameters based on a real system or are formed and validated using extensive field measurements. A range of different modelling codes are currently available able to simulate processes likely involved in leakage, e.g. PHREEQC [59], TOUGHREACT [60], PFLOTRAN [61]. The main advantage of geochemical modelling over other methods is the ability to investigate effects of leakage over large spatial and temporal scales (e.g. kilometres and decades). Investigations at these scales are necessary to understand leakage, however are challenging or even

impossible to achieve in the field or laboratory. Furthermore numerical modelling allows quantification of processes and demonstration of understanding without the logistical and operational costs associated with laboratory or field studies.

Geochemical modelling forms the most numerous method of published study, likely reflecting its convenient and accessible nature. Modelling studies for the most part have taken a generic approach. For example a recent study by Siirila et al. used PFLOTRAN [61] in combination with high performance computing to simulate leakage of CO_2 in generic shallow aquifer systems [62]. The model approach included stochastic realizations of permeability heterogeneity and calcite and galena as potential sources of lead in order to characterize potential mobilization of toxic trace metals. It was concluded that a greater level of statistical anisotropy in permeability resulted in more lateral and vertical spreading of the dissolved plume of CO_2 (Figure 9).

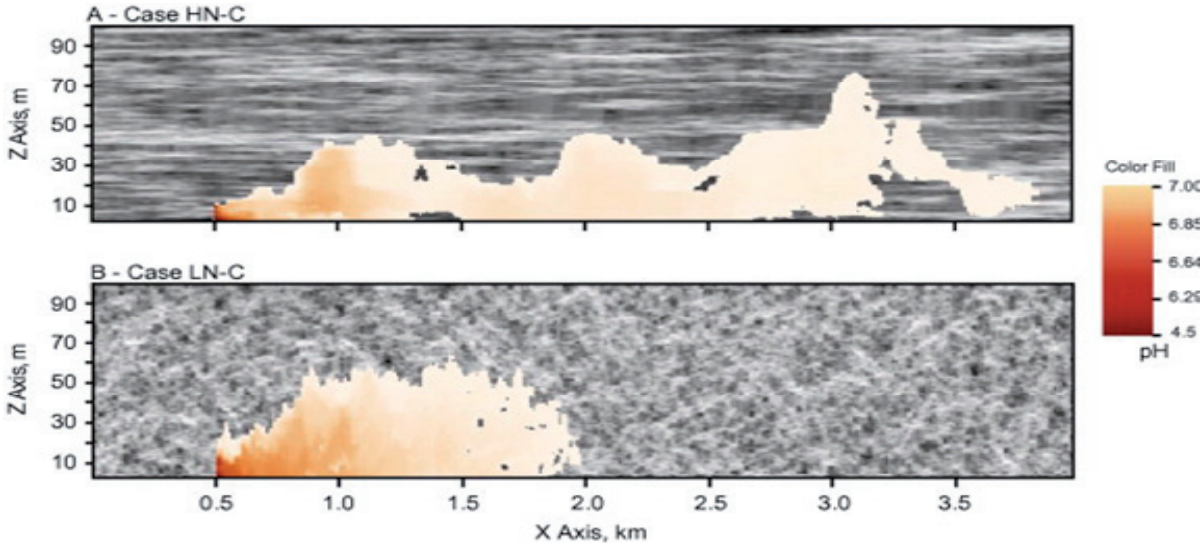

Figure 9. Snapshots in time of the pH plumes at 22 years after onset of CO_2 leakage where the down gradient wells were not pumped for one H (A) case and one L case (B). Channeling of the plume through fast velocity pathways (velocity indicated by the grey scale where white is fast pathways and grey is slow pathways) is evident in the high anisotropy case.

This in turn induced greater lead concentrations and acidification down gradient. Calcite was seen to be a more potent source of lead due to its higher solubility in comparison to galena. The study also concluded that natural

variability of various geochemical parameters, e.g. pH, can be significant. This result infers bicarbonate may actually be the most efficient indicator of leakage as CO_2 induced changes are relatively severe. Many other similar generic scenario based modelling approaches have been conducted which explore many different aquifer types, processes and potential issues providing insight into the risks associated with leakage [63-68].

Several studies directly integrate field and/or laboratory measurements within a numerical model and are consequently validated to some degree. One such integrated study used TOUGHREACT V2 to model results obtained from the CO_2 contamination field experiment conducted at the ZERT facility [69]. In this study batch style geochemical simulations were employed disregarding flow due to insufficient data and uncertainties in flow regimes. A total of 3 models were utilized implementing varying combinations of key geochemical processes; dissolution/precipitation, ion exchange and surface complexation. Results showed good approximation to field data for most parameters. Calcite derived Ca^{2+} driven ion exchange was identified as the most likely primary cause of changes in water chemistry with surface complexation negligible. Key model parameters (i.e. cation exchange capacity and distribution coefficients, sorbent quantity and site density) however were estimated and flow processes omitted limiting use in making long term predictions in space or time.

Another integrated study used a combination of mineral characterization techniques, laboratory batch experiments and numerical modelling (both batch and reactive transport) to assess processes controlling water chemistry at the CO_2 leakage natural analogue in Chimayo, New Mexico [70]. In this study the TOUGHREACT code was again employed and successfully modelled batch experiments by describing exchange/sorption processes and dissolution/precipitation reactions. During batch experiments an initial increases in arsenic was observed followed by consistent decrease. This behaviour was successfully simulated numerically and explained by precipitation of clay minerals (illite and kaolinite) and sorption. However, key model parameters were again estimated (and fitted) and no experimental proof of mineral precipitation attained, meaning exact mechanisms were inconclusive.

3.4 Method applicability and challenges

Each methodology of research plays an important role in improving our understanding of leakage. However, used individually each method has its own inherent challenges limiting applicability.

Laboratory studies form an essential investigation method allowing controlled and systematic characterization of water chemistry change likely during CO_2 leakage into shallow aquifers. This form of investigation provides an excellent starting point from which to design further more targeted and comprehensive studies, confirm understanding and support field and modelling studies. At present laboratory studies are surprisingly few with only 2 batch reactor experiments currently reported. Batch Reactors, although elegant in their simplicity, omit flow effects and are not representative of in situ conditions (i.e. sediment:water ratios) thus applicability will always be limited.

Field studies, although arguably the most applicable, still possess inherent limitations such small spatial and temporal scales in comparison to scales relevant to leakage. Heterogeneity in the field coupled to uncontrolled conditions (e.g. precipitation/recharge, preferential flow paths, varying flow direction, sample contamination etc.) also make it difficult to draw firm conclusions on geochemical processes.

Numerical models are valuable tools for assessing risk to water resources. They provide relatively limitless spatial and temporal scales, coupled to convenience and logistic simplicity. However, they usually comprise generic scenarios with few measured parameters. What limited field data may be available is also usually fitted, consequently their level of validation is usually low.

In the absence of a real leakage scenario field experiments and more specifically artificial leaks will most accurately indicate the effects of CO_2 gas in shallow potable aquifers. Field methods will always need support from laboratory methods in order to identify geochemical reactions taking place and thus are needed in parallel. Furthermore, artificial leakage experiments are essential to provide data with which to evaluate the performance of geochemical modelling codes and assure their capability. Consequently an integrated approach is clearly required whereby complimentary laboratory and field methods are employed with subsequent geochemical modelling in order to prove and quantify key processes. When conducted, these integrated studies have pushed the boundaries of our knowledge and understanding forward. However, unfortunately they are few.

3.5 Current knowledge and remaining challenges

Scientific investigations conducted during the last 10 years have begun to consolidate our knowledge regarding the effects of CO_2 contamination in shallow potable aquifers. Some key behaviors/principles are recurring within and between different sediment/aquifer types with controlling processes and concepts becoming increasingly understood, such as:

- CO_2 contamination generally results in instantaneous drop in pH, increase in alkalinity and concomitant increase in total dissolved solids (thus electrical conductivity);
- Dissolution/precipitation processes exert significant control on water chemistry changes;
- Exchange and surface processes are also involved in water chemistry changes for all sediments.
- Aquifer sediment composition and in particular carbonate content exerts dominant control on water quality changes;
- Consistent increases in some dissolved element concentrations are observed, usually those associated with carbonates, i.e. Ca, Mg (but also K and Si) and other substituting minor cations (e.g. Sr, Ba);
- Groundwater flow is an important factor effecting development of water chemistry;

These clear and concurrent observations allow us to begin answering the key questions regarding leakage of CO_2 into shallow aquifers. However, unfortunately some results are not concurrent (i.e. trends are contradicted between studies) or comprehensive (some parameters omitted or not considered) inferring our understanding is incomplete, such as:

- The complete range of sediment types and range of hydrogeological conditions likely affected by leakage have not been investigated;
- Erratic/inconsistent behavior of dissolved trace element concentrations and redox sensitive species is observed (e.g. Al, Ni, Cu, Zn, Fe, Mn) inferring mobilization is poorly understood;
- Geochemical process contribution to water chemistry change is poorly understood;
- Applicability of some methods to real leakage is low and poorly understood;

- Temporal and spatial scales investigated have been limited;
- Effects of flow are paramount and are currently poorly characterized or understood;
- Numerical models are mostly generic with little or no validation thus accuracy in time and space is uncertain;

Until these issues are addressed it will be difficult to fully assess risks to water resources posed by leakage and subsequently design adequate monitoring, measurement and verification (MMV) programs in order to detect leakage.

4 Objectives

This thesis aims to answer the two key questions regarding leakage of CO_2 from CCGS into shallow potable aquifers, namely:

- What are the risks to shallow groundwater resources posed by leakage?
- How can leakage be detected geochemically?

As previously described singular investigation methods face significant limitations in applicability and scope, thus an integrated approach employing all 3 investigation methods was employed. This ethos would minimize limitations, allowing comprehensive assessment of risks posed to water resources to be made and the most effective way to detect leakage geochemically to be determined.

The objectives of the study are thus:

- Use laboratory methods to assess risks posed to shallow groundwater quality by leakage and to support field studies;
- Conduct a sustained CO_2 physical leakage simulation in a shallow potable aquifer to determine risks posed and most efficient methods of detection;
- Numerically model field and laboratory results in order to confirm and improve understanding of processes occurring; and
- Create a validated reactive transport model from which predictions and scenarios can be explored.

Finally, although a site specific case study it is a key objective that conclusions drawn are applicable to other sites with key fundamental phenomena associated with CO_2 contamination identified.

5 Results

5.1 Vrøgum field facility

In order to conduct a field scale shallow aquifer leak simulation from which to assess risks to water resources and determine suitable MMV detection parameters, a field site was required. Several clear requirements were identified for the field site in order to make the experimental design, set up and operation as efficient and effective as possible. Requirements included: a realistic potable aquifer system, simple hydrogeology (in terms of flow and recharge), relatively homogenous sediment, safe distance from large populations (for both security and safety reasons) and a scientifically interesting mineralogy. These requirements would also ensure meaningful interpretation of results was achievable.

Several areas were first pursued before selection of an area close to Oksbøl, western Jutland which fulfilled most requirements. The chosen study area is a silicate dominated, unconfined shallow aquifer system containing potable quality water. After approximately 1.5 years of negotiations, permissions were granted by Varde Kommune (local government authority) for drilling investigations and CO_2 injection. Subsequently field characterization campaigns were implemented and experimental infrastructure installed.

Vrøgum is a managed forest plantation 3 km from the Danish west coast (Fig.10a) and the field site comprises a grassy clearing approximately 165 m by 40 m within which is a small ephemeral pond (Fig. 10c). Lithologically (Fig. 10b) the site is comprised of a 5 – 6 m layer of aeolian sand (including a 0.2 m layer of topsoil) underlain by approximately 5 – 6 m of glacial sand with some gravel. At the interface of the two layers a highly gravelly zone is present of approximately 0.3 – 0.5 m thickness. Underlying the two upper layers, a 50 m thick formation of medium marine sand is present followed by clay at around 60 m depth. The Vrøgum unconfined sand aquifer has a shallow water table, approximately 1.5 – 2 m below ground level and is located close to a groundwater divide. Consequently hydraulic gradient is low (0.0014) and flow direction varies (195◦ and 185◦ in north western and south eastern area domains respectively) (Fig. 10c).

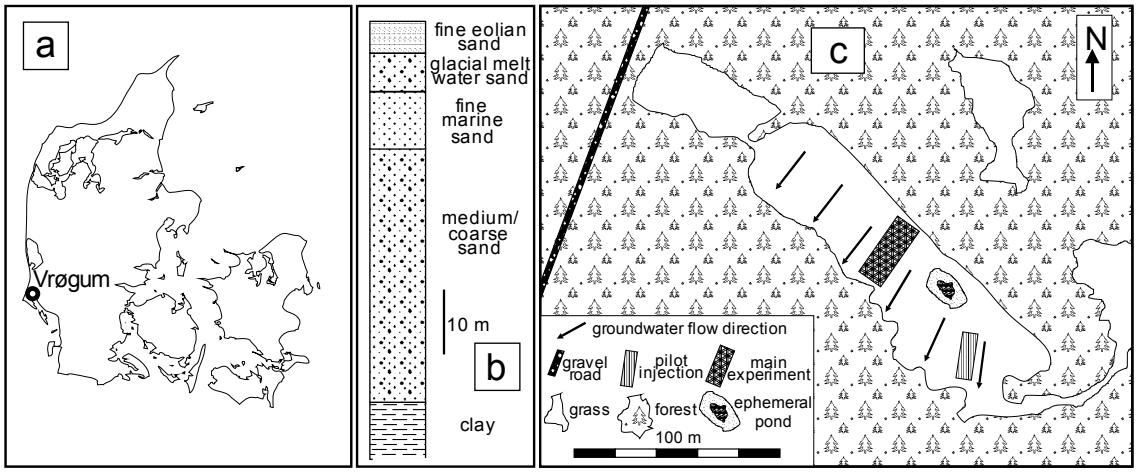

Figure 10. a) map of Denmark with field site location shown, b) a generalized geological profile, c) a close up map showing the main features and the groundwater flow direction.

The field investigations described herein focus on the upper part (0 – 12 m depth) of the Vrøgum aquifer, i.e. aeolian and glacial sand layers (Figure 11). The aeolian sand (approximately 0 – 6 m depth) is composed primarily of quartz with some feldspar, plagioclase and clay whilst the glacial (approximately 6 – 12 m depth) is also formed primarily by quartz with some feldspar and plagioclase only. Natural hydrochemistry reflects the inert silicate dominated mineralogy (i.e. acidic, little to no alkalinity and very low TDS) with slightly distinct groundwater chemistry observed between layers. The aeolian and glacial sands appear chemically similar in terms of major and minor dissolved ions however show subtle redox differences, likely reflecting the mineralogy/sediment content and flow conditions. The aeolian sand exhibits slightly lower DO and slightly higher alkalinity. This likely reflects the low levels of organic matter and silt present indicating organic matter degradation (i.e. depleted O_2 and elevated CO_2 implied by higher alkalinity) and slow groundwater movement/low permeability. In contrast the glacial sand is characterized by higher levels of DO with little to no alkalinity reflecting the absence of organic matter and relatively faster flowing oxygenated water.

More detailed descriptions of the site and study formations are given in papers II and III or where appropriate in the proceeding sections.

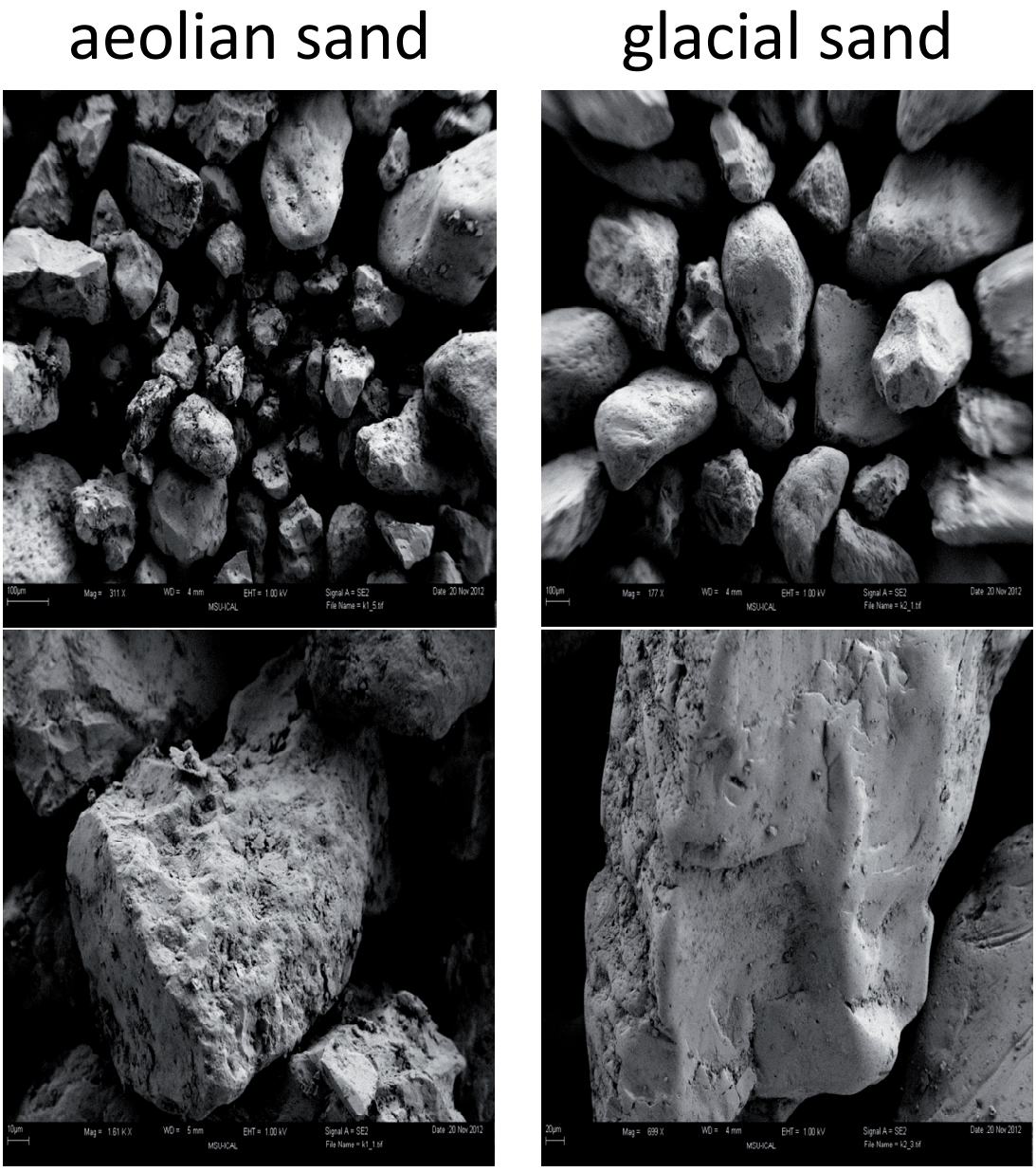

Figure 11. SEM micrographs of aeolian and glacial sand grains. Scales are given in the bottom left corner of micrographs. Note generally smaller grain size of aeolian sediment and presence of clay in comparison to glacial sand.

5.2 Laboratory experiments

Laboratory studies were employed as a key method in this Ph.D. investigation as both stand alone investigations and to aid design and interpretation of field investigations. Laboratory work included: batch reactor style experiments; a flow tank experiment and comprehensive mineralogical studies.

5.2.1 Batch experiments

Using a similar method to previous published studies [46-47], a series of simple batch reactor experiments were conducted. The experimental setup was simple, involving glass flasks containing sediment water mixtures of varying ratios exposed to CO_2 with water chemistry change subsequently monitored (Figure 12). The aim of these simple tests was to attain basic measurements and information on the chemistry changes that would potentially occur in the field and during a real leakage scenario. Two full batch investigations were conducted; a site specific Vrøgum sediment study and a general Danish sediment study.

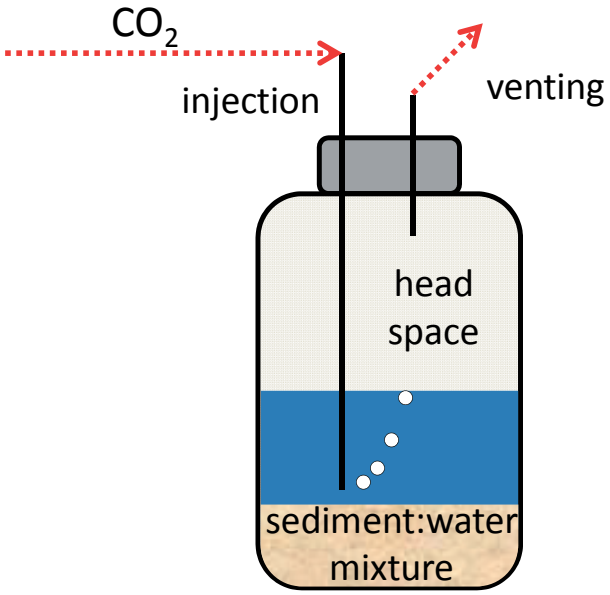

Figure 12. Batch reactor set up.

Vrøgum Batch Reactors

A series of batch experiments were conducted on Vrøgum sands in order to investigate reactivity of sediment layers and thus assess suitability for field study. During these experiments the effects of gas phase CO_2 on water chemistry using various sediment:water ratios, time scales and initial solutions were studied. Full details including results are given in technical report I. Batch experiment initial solution composition and methodology can differ vastly from aquifer conditions (i.e. sediment:water ratios and use of deionized water) which is an issue highlighted as limiting applicability and validity of such methods [71]. The variety of batch reactor set ups considered here provides a unique opportunity to address these issues. Furthermore re-

sults can ultimately be compared to field injection results forming a valuable resource with which to answer questions of applicability. Consequently this issue is addressed more comprehensively in the discussion. Results confirmed field site sediment would react suitably to CO_2 contamination with acidification of 1 pH unit and increases in most dissolved ion concentrations observed in all reactor set ups. Results also showed reactor set up, and in particular the use of de-ionized water, exerts a subtle influence on results.

Danish Sediment Batch Reactors

A range of sediment types forming shallow potable aquifers or strata they are likely in contact with from across Denmark were also investigated by CO_2 batch reactors. A full description of this study including methodology is given in Paper I. The aim of the study was to build upon previous work conducted and further characterize factors controlling water chemistry evolution. In particular the effects of varying carbonate content on water chemistry were explored. Results demonstrate clear control on water chemistry evolution by sediment mineralogy. Most significant control on water chemistry was seen to be caused by carbonate content, for which a potential semi logarithmic relationship with pH and alkalinity was observed (Figure 13). In addition control of water chemistry by calcite equilibrium was also inferred for sediments containing > 2% inorganic carbon, whereby a pH minimal of 6 and alkalinity maximal of 20 meq/l were observed. In general sediments could be divided into three categories based on water chemistry response to CO_2 contamination; carbonate dominated (i.e. >2 % TIC), Silicate dominated (<2% TIC) and mixed (clay, carbonate and silicates mixtures). Carbonate dominated and mixed sediments showed the most severe changes in water chemistry with large increases in aqueous element concentrations coupled to minimal reductions in pH due to high buffering capacity. Silicate dominated sediments exhibited small changes in major ions however were subjected to the greatest reductions in pH, displaying propensity to mobilize high toxicity pH sensitive trace species. Based on this assessment the sediments types described each pose unique risks to water quality, possessing different hydro-chemical responses that should be incorporated into MMV programs in order to detect leakage. In sedimentary basins targeted for CCS there will likely be a combination of these sediment types within the geologic profile (including heterogeneities within strata) in addition to flow which will increase the complexity of geochemical reactions.

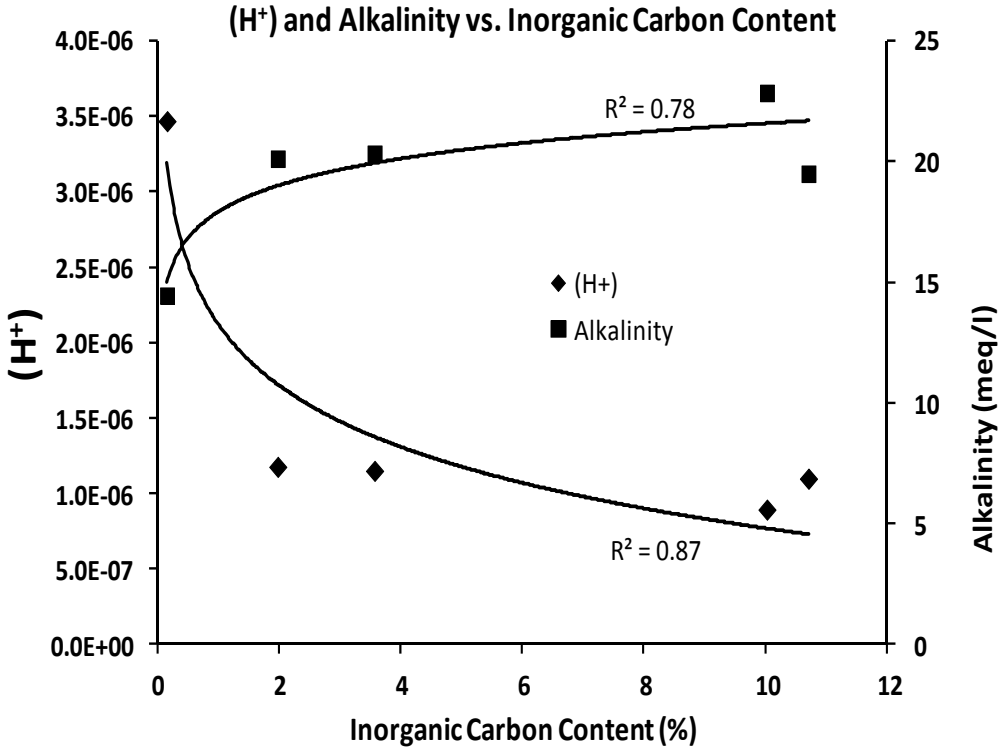

Figure 13. Maximal proton activity and Alkalinity vs. inorganic carbon content for Danish batch reactor studies (from Paper I).

5.2.2 Flow tank experiment

Due to the limitations of batch style experiments, a flow tank was designed and constructed using Vrøgum sediment. Mixed aeolian and glacial sands were employed in a flow system using natural groundwater. Following establishment of a stable baseline flow and chemistry, CO_2 was injected continuously into the sediment for 52 days and water chemistry evolution monitored with flow. The aim of this experiment was to create flow conditions comparable to the field site on which the effects of gas phase CO_2 could be observed. By observing the effects of CO_2 induced acidification with flow further insight into how the target shallow aquifer would respond to injection of gas phase CO_2 could be gained. Results were subsequently used to aid design of field experiments and interpret results. Furthermore this experiment forms an interesting standalone investigation the likes of which has not been reported in the literature previously. Selected results and interpretation are given in technical report II. The flow tank clearly showed flow exerts significant influence on water chemistry evolution, giving rise to distinct spatial and temporal development. This development is not captured using batch style experiments which ignore flow or field studies which do not inject continuously

over significant periods of time. The effects of flow were manifest as an initial pulse of elevated dissolved elements (Na, Ca, Mg, Si and to a lesser extent Sr) and alkalinity which dropped towards background levels by the end of the experiment. Acidification conversely was persistent, being maximal close to the injection reaching the lowest pH value observed around 50 days, before apparently stabilizing. At sample points 0.25 and 0.45 m down flow, pH continued to decrease until the end of the experiment seeming to approach similar levels of acidification induced adjacent to the injection (Figure 14). This pulse phase effect which has been observed and described once previously [72] appears a key part of chemistry evolution during leakage of CO_2 into shallow aquifers. Consequently it has significant implications for risk assessment and MMV program design, therefore understanding of its underlying causes and continued evolution is paramount and would be addressed further in field investigations.

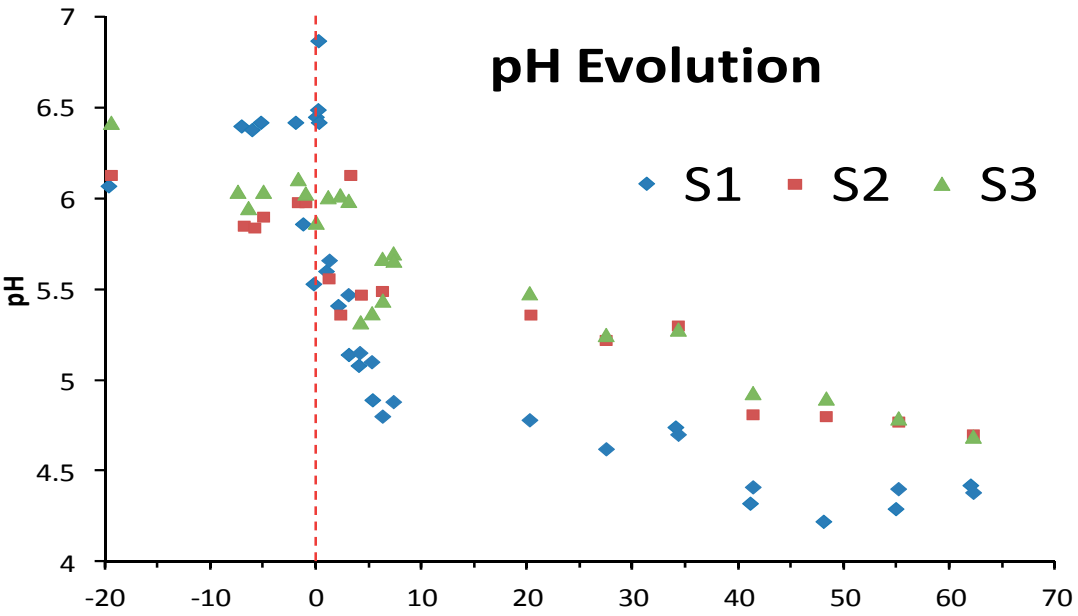

Figure 14. Evolution of pH vs. time (in days) in Vrøgum sediment flow tank 0.05, 0.25 and 0.45 m (S1, S2 and S3 respectively) down flow of the CO_2 injection (Technical Report II). Red dotted line indicates beginning of CO_2 injection.

5.3 Field experiments

5.3.1 Pilot injection

During field experiment planning and design a pilot CO_2 injection was conducted in order to test the field site conceptual model, assess aquifer response

and prove injection/sampling methodologies were effective. The pilot experiment was conducted in October 2011 and is presented in full in paper II. A simple, small scale field injection of gas phase CO_2 was conducted in the south east part of the field site employing 17 multilevel sampling points (2.4, 4 and 8 m depth). Following a background monitoring period, 45 kg of CO_2 gas was injected at 10m depth into the glacial sand via an inclined injection well through a porous sparging screen. Water chemistry was subsequently monitored with decreasing frequency over 126 days providing the first in situ measurements on the effects of CO_2 contamination at Vrøgum. First and foremost the results showed injection and sampling methodologies were efficient and site conceptual model adequate. In addition to this results also gave an indication of chemistry evolution likely during the main experiment and in the event of a real leakage scenario. Although only 48 hours of injection were implemented, effects of dissolved CO_2 (inferred as increased electrical conductivity and elevated ion concentrations) were evident 56 days post injection in the first sample points. Dissolved CO_2 was not at any stage detected in the aeolian sand layer inferring migration was prevented by differences in permeability. Elevated ions (Al, Ba, K, Na, Mg, Si, Sr and Zn) and EC were seen to move with advective flow and eventually flush from the monitoring network. Persistent and continuing acidification however was still evident 126 days post injection, inferring lasting effects on the sediment. The most stable and reliable indicator for dissolved CO_2 in this short duration experiment was clearly EC whilst pH was seen to be relatively unstable. A natural fluctuation of pH was observed prior to and after injection making it challenging to fully delineate the effects of CO_2 from natural variation. Overall changes in water chemistry were small and consequently risk to water resources from this very short duration test experiment low. However, two potential concerns were identified; potential accumulation of elements with flow and continued acidification caused by buffering exhaustion. Both of which would be investigated further in the main experiment.

5.3.2 Main release experiment

The main release experiment was the key focus of the Ph.D. project around which laboratory and field investigations were centered. As previously described, in lieu of an actual leakage scenario the most realistic and applicable way in which to assess the risks posed by and how to detect leakage is by physical simulation on a relevant scale. The aim of the main experiment was thus to perform continuous injection of gas phase CO_2 into the Vrøgum aqui-

fer and monitor water chemistry evolution over significant temporal and spatial scales. Based on laboratory and field work conducted over the preceding 1.5 years, an experiment was designed whereby a total of 1600 kg of gas phase CO_2 was injected at 5 and 10 m depth over 72 days through 4 inclined injection wells (Figure 15). Water chemistry was monitored for physical and dissolved element evolution through an extensive network of 30 multi-level sampling points over 305 days. In addition to monitoring water chemistry evolution, sediment cores were taken pre and post injection and analysed to determine effects of CO_2 contamination on mineralogy and sediment properties. The leakage simulation took place between 14th May and 24th July 2012 providing a total of 72 days of continuous injection and analysis of more than 778 water samples. Results and full details of the methodology are given in paper III.

Figure 15. Modified Geoprobe (model 7822DT) drilling main experiment 45 degree inclined CO_2 injection well at Vrøgum field site. Inclined injection wells were employed to enhance dissolution and dispersion of CO_2 into groundwater and limit migration along injection piping.

Results showed the physically simulated leak evolved in two distinct phases; an advective pulse (characterized by increased aqueous ion concentrations

and EC) succeeded by increasing persistent acidification (gradual and sustained decrease in pH). Spatial and temporal differences in evolution of these phases suggest separate geochemical mechanisms and signatures with implications for environmental risks and leak detection. Aqueous element concentrations developed exhibiting 4 behaviors; 1. advective pulse (Ca, Mg, Na, Si, Ba and Sr,), 2. pH sensitive/abundance dependent (Al and Zn), 3. complete removal (Mn and Fe) and 4. unaffected (K). Concentration behaviors were characterized by; 1. a maximal front moving with advective flow, 2. continual increase in close proximity to the injection horizon, 3. removal from solution to zero concentration and 4. no significant change. Only Al was observed to exceed WHO guideline levels, however significantly so (10 fold excess). Significant control of water chemistry by gibbsite equilibrium was proposed. Pre and post injection sediment analysis showed significant alteration of sediment composition and properties including depletion of reactive mineral species. Accumulation with flow was not observed.

5.4 Geochemical modelling

Following conduction of the extensive laboratory and field studies described, a geochemical modelling investigation using PHREEQC [59] was undertaken. The aim of the modelling study was to test understanding of geochemical processes and quantify CO_2 induced water chemistry changes. The modelling study would also allow the ability of PHREEQC to describe the effects of CO_2 contamination to be tested. The modelling study and its results are presented in paper IV. The glacial sand was chosen as the target of the modelling study due to its relative homogenous nature and consistent water chemistry response to CO_2 contamination. As such comprehensive characterization of the glacial sand undertaken during the field studies was used as a basis on which to build the model. A simple 1 dimensional reactive transport model including gibbsite derived (amorphous and crystalline forms) Al driven (fitted) ion exchange (based on laboratory results) was able to simulate the majority of water chemistry evolution observed in the field over the most significant temporal and spatial scales. The model suggests gibbsite dissolution leads to Al driven ion exchange which is the underlying cause of the pulse effect observed at Vrøgum (Figure 16). Sediment depletion also takes place whereby reactive minerals (i.e. amorphous and crystalline gibbsite) are dissolved, flushed and ultimately exhausted causing increasing and persistent acidification. Consequently zones of acidification succeeding the pulse are created with a zone of maximum acidification slowly radiating out from the

injection plane. In this acidified zone dissolved element concentrations return towards background levels (including alkalinity) thus may not be suitable parameters for leak detection. Dissolution of other pH sensitive minerals (if present) may now occur releasing other potentially dangerous elements and/or surface bound amphoteric elements.

In addition to the flow model a batch version was also formed simulating a reactor experiment described in technical report I. The batch model employed the same processes and sediment parameters and was most accurately able to simulate observed results, further supporting model composition.

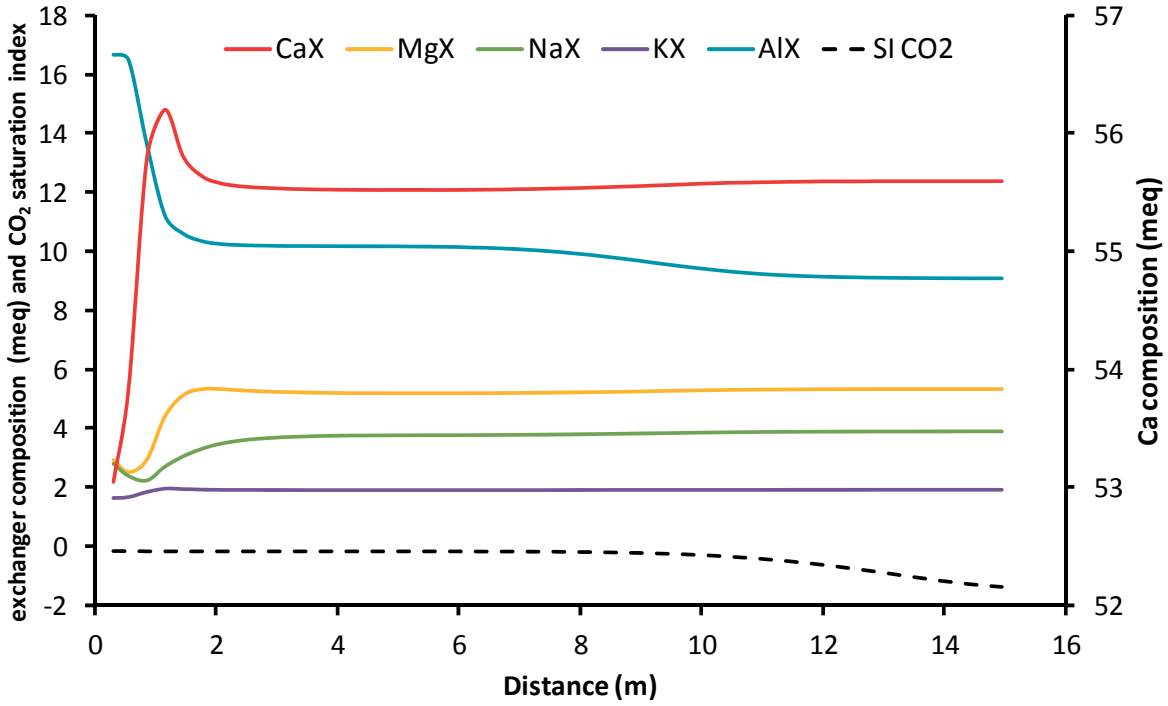

Figure 16. Reactive transport model cell exchanger composition with distance after 65 days of simulation showing CO_2 induced gibbsite dissolution causing exchange of Al^{3+} for other elements as the key driver of water chemistry change.

The validated reactive transport model was subsequently used to make longer term predictions and explore various scenarios including increases in depth (i.e. increased P_{CO2}) and varying calcite content. Assuming constant and stable leakage of CO_2, long term predictions suggest the zone of increased acidification would grow indefinitely, eventually becoming 100's or 1000's of meters in size. The long term model also suggests a secondary peak of dissolved elements may form at the interface of buffering exhaustion. This peak

is caused by hydrodynamic dispersion and occurs where inflowing CO_2 charged groundwater travels through depleted aquifer sediment and reaches sediment with remaining buffering capacity. Once acid groundwater encounters sediment containing gibbsite, dissolution is induced followed by ion exchange inducing the observed peak. Although potentially observed (based on late time field measurements) this process was not proven and requires further investigation in order to verify it as a real effect. Increasing depth suggests buffering exhaustion (i.e. dissolution of gibbsite) would be more rapid. This would induce greater pulse peaks of dissolved elements (via Al driven ion exchange) and increased, more rapid acidification suggesting risks to water resources increase with depth. Addition of calcite to the model provides additional buffering capacity limiting acidification. However, calcite dissolution induces additional Ca driven ion exchange and consequently water chemistry change is generally more severe. Higher pH's however are maintained so would presumably limit mobilization of amphoteric and pH sensitive species. Although a site specific modelling study, all effects and processes observed have clear and significant implications for risks to silicate based aquifers during leakage from CCGS.

5.5 Montana investigations

Two investigations were conducted regarding risks posed to groundwater resources by leakage from CCGS in association with the Energy Research Institute, Montana State University; 1. hydrogeological assistance was provided for Kevin dome storage project and 2. an investigation to assess if sediment depletion has occurred and can be detected at ZERT field facility was undertaken.

5.5.1 Kevin dome storage project

Kevin dome storage project is a proof of concept carbon sequestration project, currently in the planning stage, being undertaken by the Big Sky Carbon Sequestration Partnership (BSCSP) in northern Montana. Approximately 1 million tonnes of CO_2 will be abstracted from Kevin Dome (a natural CO_2 trap) then re-injected into the adjacent Duperow formation in order to assess and prove feasibility of widespread implementation of CO_2 sequestration in northern Montana (Figure 17). As part of the project a class VI injection well permit is needed which requires (amongst other things); identification and characterization of all underground stores of drinking water (USDW's) over-

lying the storage reservoir, determination of baseline chemistry for all identified USDW's and characterization of hydrogeology (including flow regimes and hydraulic properties). Ultimately it is necessary to demonstrate a thorough understanding of the site in order to design an adequate MMV program and attain full permissions for the project.

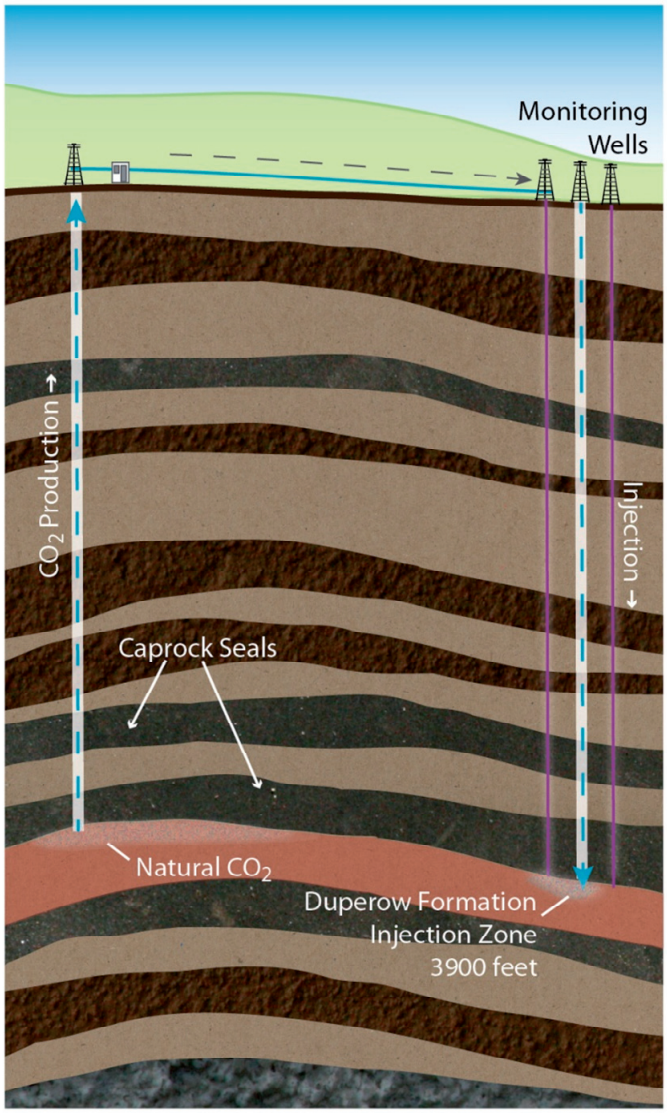

Figure 17. Schematic of Kevin dome storage project showing abstraction and reinjection of CO_2 and overlying aquifers which would be at risk from leakage.

A key aim of the external research stay was thus to apply the knowledge and understanding of issues relevant to CCGS leakage gained during the Ph.D. program to a full scale, real storage project.

Firstly a desk study using available databases was conducted with relevant information attained, collated and interpreted. USDW's were then identified, characterized (hydrogeologically and hydrogeochemically) and recommendations subsequently made regarding implementation of a suitable MMV program. Risks to water quality were also assessed and desirable further work suggested. In addition simple geochemical modelling using PHREEQC was conducted to identify minerals likely present (inferred by saturation) based on average background water chemistry. Subsequently changes in saturation likely following CO_2 contamination were determined by imposition of 1.5 bar P_{CO2} on average USDW chemistry thus indicating potential dissolution/precipitation reactions which may occur. The results, conclusions and recommendations given in the report should; aid a thorough understanding of the natural hydrogeological regime present, contribute to the success of the permitting process and further general progress of the project. The Kevin Dome report is presented in full as additional information accompanying the thesis (in electronic form only).

5.5.2 ZERT core study

The ZERT field facility operated by Montana State University, Bozeman was the first experimental field facility constructed to investigate leakage of CO_2 from CCGS [48]. Furthermore it was the first facility to describe the in situ effects of CO_2 contamination on groundwater chemistry [49] as previously described in section 2.2. The field facility comprises 100 m of perforated horizontal steel pipe at 2-3 m depth in the Bozeman alluvial fan, forming 6 individual injection zones (each flow controlled) separated by a packer system. Zone 6 is a 10 m section of perforated screen around which groundwater monitoring wells were installed. Although only one study season has been published, CO_2 has been released into the subsurface through this zone each summer since 2007. In total, 3749.5 kg of CO_2 have been injected through zone 6 over a cumulative total of 149 days. The annual injections through zone 6 mean the adjacent alluvial sand and gravel sediment has been exposed to a significant level of CO_2 charged groundwater flow. This makes ZERT an excellent case study on which to determine the potential effects of leakage on aquifer sediment composition. Consequently during the external research stay a core study was undertaken whereby 4 cores were drilled along the flow line at varying distances from the injection screen in order to determine the effects of CO_2 (if any) on the sediment. Selected results and more detailed description of the study are given in technical report III. Cores were taken 1.5, 5

and 10 m down gradient from the injection screen with an additional control core taken 20 m up gradient. Sections of core (from 1.9 - 2.1 m depth) were analysed by a suite of laboratory methods to characterize sediment composition and physical properties in order to determine if effects of prolonged contact with CO_2 charged water were evident. Results show cores were generally comparable in terms of composition and properties with no conclusive differences between CO_2 affected (i.e. down gradient) and control (i.e. up gradient) samples. Some weak trends were observed down gradient and with distance from the injection screen, however these were generally counterintuitive, e.g. increases in more reactive minerals adjacent to the injection. The highly heterogeneous nature of the ZERT sediment (i.e. tertiary deposits consisting of conglomerate, sandstone, siltstone, and claystone deposited in a fluvial environment) infer identifying the effects of CO_2 charged groundwater may be challenging. Consequently more detail on the level of heterogeneity is required in order to interpret results. Nonetheless it is surprising that following injection of 3749.5 kg of CO_2 over 149 days that no clear difference between cores can be delineated. In summary results were inconclusive and highlight the need for further investigations regarding the potential long term effects of CO_2 leakage on shallow aquifer sediments of mixed and carbonate dominated composition.

6 Discussion

6.1 Applicability of methods

An issue of contention regarding research on the effects of CO_2 contamination in shallow potable aquifers is applicability. Exactly how leakage would manifest is unknown however it will likely not be the same as methods currently employed in the literature. This is particularly pertinent for laboratory experiments and in particular batch reactor studies which are arguably the least applicable method currently employed. This issue of contention has previously been debated with vigour [71, 73] and raises important questions. The main issues regarding applicability of batch reactors studies are; scale, methodology (i.e. sediment:water ratio, disaggregation of sediment, enhanced mixing, use of deionised or synthetic groundwater) and varying kinetics under laboratory conditions inferring results may be misleading or exaggerated. Therefore a key issue to clarify is how applicable laboratory methods are to a real leakage scenario or at least to in-situ field studies. Furthermore the applicability of field studies is also questionable, at least regarding temporal and spatial scales studied. Scales needed to accurately assess effects of leakage are not known, however it is essential scales studied are sufficient to observe all chemistry evolution following CO_2 contamination. The work conducted as part of this Ph.D. study may not fully answer these important questions however it does form a very valuable resource. Not only are stand alone investigations described exploring the effects of CO_2 on water chemistry independently, but multiple methods have been employed on the same sediment, i.e. Vrøgum sands. During this Ph.D. investigation methodologies utilizing Vrøgum sediments include: multiple CO_2 exposure batch reactor studies, a laboratory flow tank study, a short duration pilot field injection and a larger scale sustained field leak simulation. Consequently comparison of the results should indicate how comparable methods are and thus infer applicability.

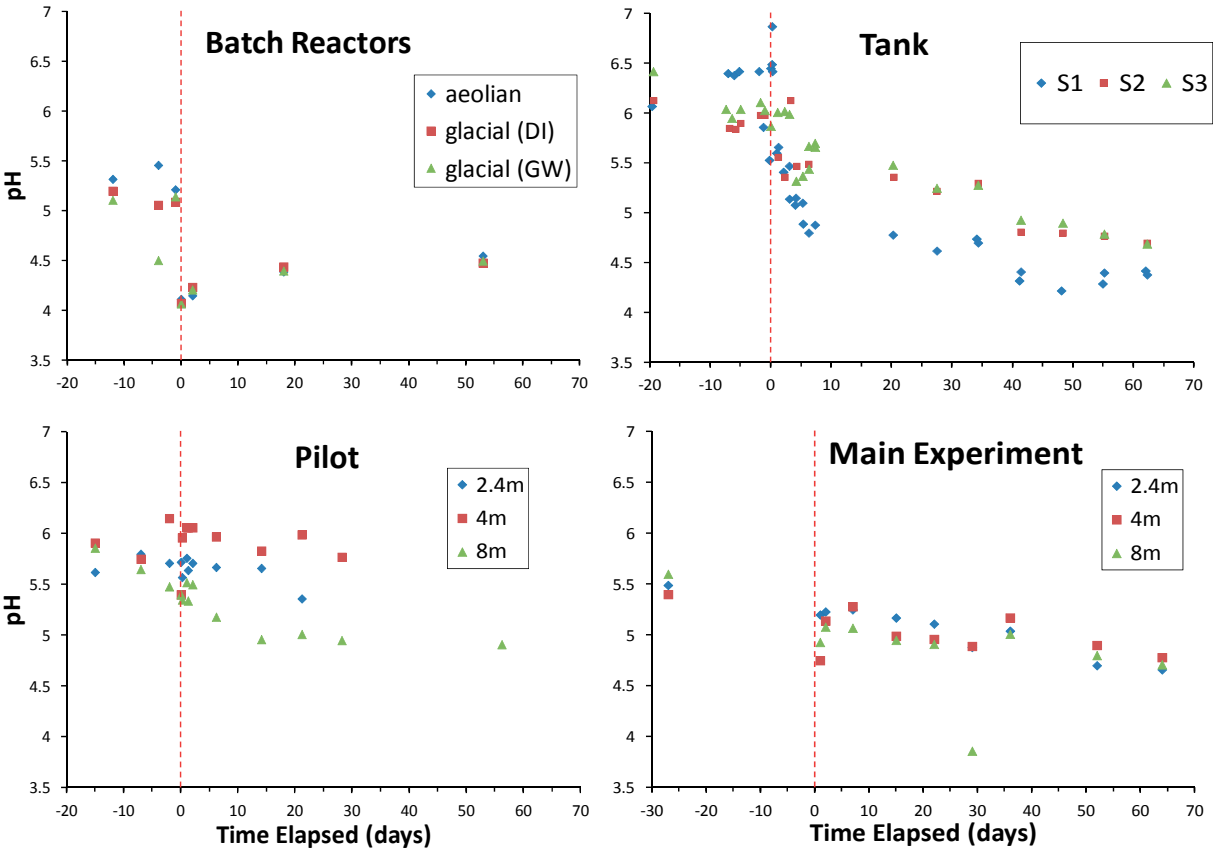

Figure 18. Comparison of pH development with time for different methods employed in this Ph.D. study. Red dotted line indicates CO_2 exposure. For details on methodologies the reader is referred to the relevant detailed study description. Pilot and main experiment series displayed are by depth and for sample points 0.5 m and 1.5 m down flow of injection respectively.

Clear variation of pH development following CO_2 injection between methods is evident (Figure 18). However, considering the significant differences between methodologies (i.e. 30 minute batch injection compared to a 72 day in-situ injection) results could be considered to be relatively comparable. Batch reactors exhibit what seems to be the most severe level of acidification almost immediately whilst other methods move towards this level during their later stages. The slower and less severe acidification observed in the flow based studies (i.e. tank and field injections) likely reflects additional buffering capacity provided by the higher sediment:water ratio and absence of disturbance/mixing. Thus it can be concluded batch reactors exaggerate the level of acidification likely in the field however only by a small degree. It should be noted pH almost falls to batch levels in the tank experiment (close to the injection screen) and is still decreasing at the end of the main experiment suggesting batch reactors could potentially provide information on a worst

case scenario, i.e. determine a maximum level of acidification likely in the field.

Comparison of Ca and Al concentrations observed between the various methods is shown in Figure 19. Concentration comparison for Ca shows clearly the effects of flow with distinctive pulse behaviour particularly for the tank but also for field experiments (as described in paper III and technical report II). Batch reactor Ca concentrations do not capture this behaviour but exhibit a steadily increasing plateau underestimating field and tank results (significantly so for the latter). Tank results are particularly high which may be a consequence of mixing of aeolian and glacial sands coupled to laboratory enhanced kinetics. Groundwater batch reactor Ca results are comparable to field observations inferring this method is applicable, at least to some degree. However, de-ionized water batch reactors significantly underestimate Ca increases. Either way results for Ca (which were seen to be typical for Na, Mg, Si, Sr and Ba also) are quite variable between methods inferring quite different conclusions may be drawn.

Concentration of Al follows a pH/abundance dependent behaviour and exerts significant influence on water chemistry evolution as described in papers III and IV. Comparison of Al development between the various methods is of particular importance for Vrøgum and shows clearly significant variation. Al concentration development for some of the methods and sample points (i.e. flow tank sample point S2 and S3 and pilot and main injection 8 m depth sample points) are relatively similar and indicate little or no risk to water resources. Development in some other methods and sample points however shows a significant risk to water resources with Al concentrations reaching 5 – 10 times the WHO limit of 5µmol/l (i.e. ground water and de-ionized water batch reactors, tank sample point S1 and main experiment 2.4m depth sample point). Flow based experiments exhibit a gradual increase (slightly erratic for field methods) whilst batch reactors show immediate increase followed by a plateau. Clearly the highest concentration observed is for the main experiment (2.4 m depth sample point) which is likely a result of abundance of gibbsite at shallower depths as described in paper III. This result would have been missed using the other methods alone however batch reactors do actually provide some insight to what may be the worst case.

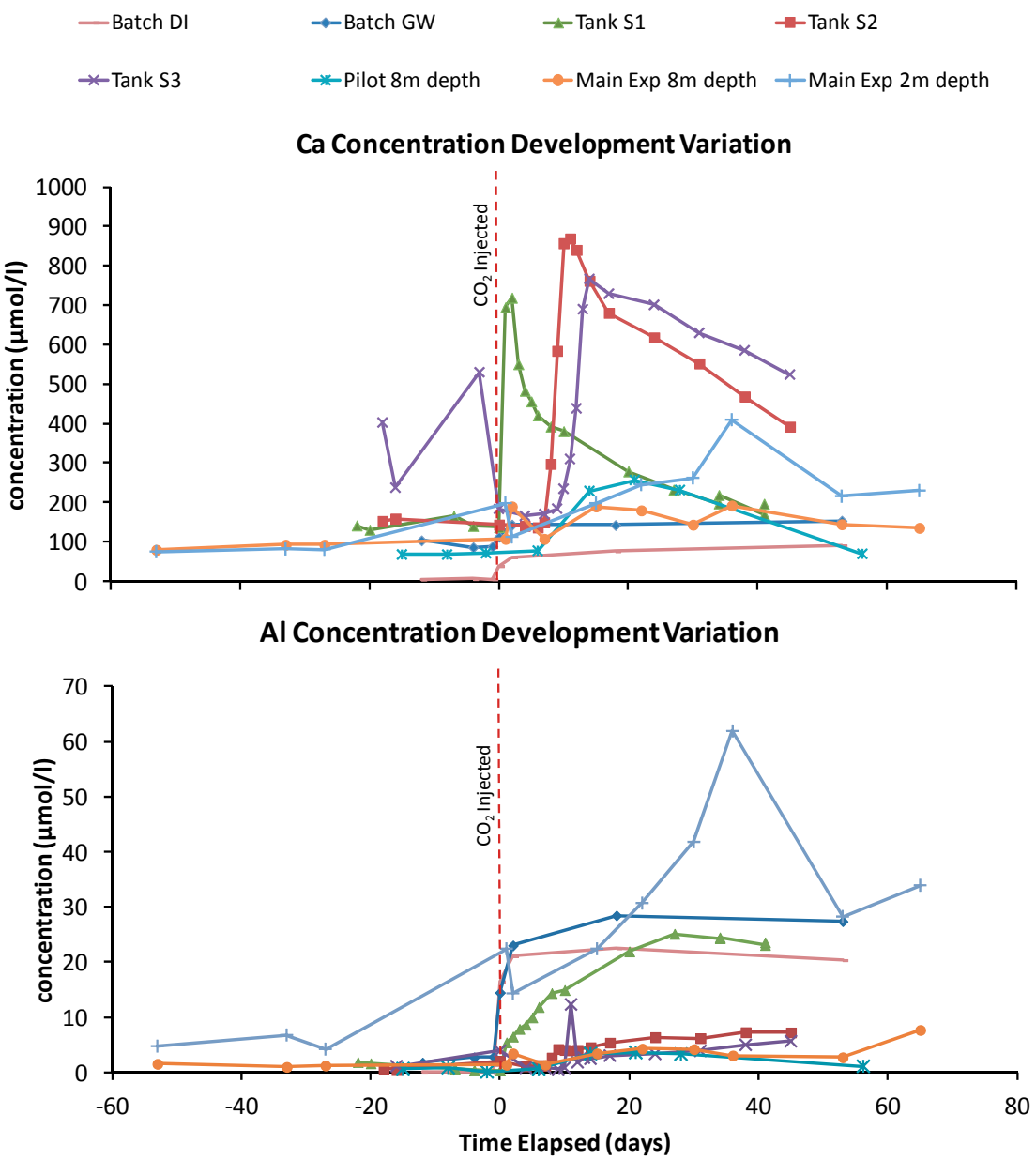

Figure 19. Comparison of Ca and Al concentration evolution for various methods employed in the Ph.D. investigation using Vrøgum sediment.

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It is essential the applicability of methods employed is understood to allow risks to water resources to be assessed accurately and with confidence. The work reported in this thesis has hopefully provided some insight to this very important issue. However, this brief comparison of results is not comprehensive and merits more consideration in order to understand the cause of differences, the scope of which is unfortunately beyond this Ph.D. study.

6.2 Risks to water resources

From the work described in this thesis it is clear that assessment of risks posed by CO_2 leakage from CCGS into shallow potable aquifers is not a simple matter. The Danish and Vrøgum sediment batch experiments (Paper I and technical report I) clearly show the overarching control exerted by sediment mineralogy and highlight heterogeneity within a formation (even over small scales) influences risks posed. Results show sediment composition should be the first and foremost consideration of risks posed, a concept which is well reported [47]. Sites must be considered in a specific manner however generalization, at least to some degree, is highly desirable to allow preliminary risk assessment to be conducted. The work conducted in paper I showed a general level of risk could be delineated into 3 sediment groups; silicate dominated, carbonate dominated and mixed. Level of risk is not progressive between categories, rather distinct. Carbonate dominated systems (>2% TIC) exhibit severe water chemistry change in response to CO_2 contamination, however this is mostly limited to non-toxic carbonate related cations. Furthermore high buffering capacity prevents significant acidification, likely preventing mobilization of pH sensitive trace metals should they be present. Silicate dominated sediments (< 2%TIC) show only subtle changes in water chemistry post CO_2 exposure with small increases in major ions associated with sili-

cate minerals and exchange processes. Acidification in this type of formation however will be significant (increasing with decreasing TIC, i.e. 2 – 0 %) inferring potentially toxic pH sensitive trace metals (if present) could be mobilized. Finally mixed sediments (containing silicates, carbonates and clay minerals) generally observed the most deleterious water chemistry development with a broad range of major and minor (potentially toxic) ions being mobilized. Although mixed sediments possess significant buffering capacity increased dissolution and ion exchange combine to degrade water quality significantly. These mixed composition formations may not be used for potable water abstraction exclusively however will be present in sedimentary basins considered for CCGS thus must be considered in risk assessment. In reality a combination of formation types will exist within a geologic profile overlying a potential storage reservoir, thus assessment of risk becomes more complex (Figure 20).

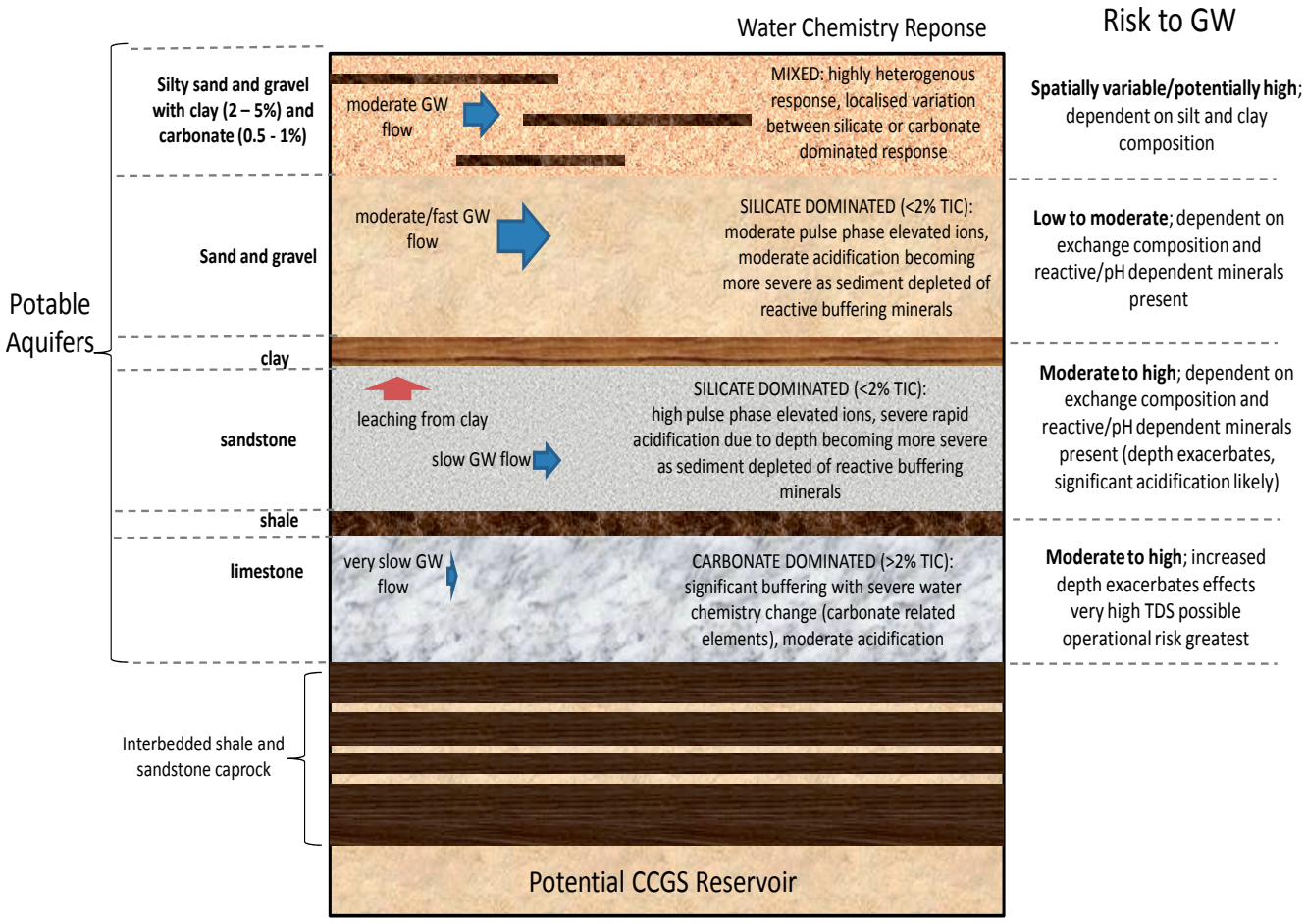

Figure 20. Typical geologic profile of sedimentary basin overlying potential CCGS reservoir. Schematic highlights complexity of risk assessment with variation of risk to water resources from leakage based on concepts concluded from Ph.D. studies.

The flow based investigations presented in this thesis (Papers II – IV and technical note II) focus on a silicate dominated aquifer system, thus can only infer risks associated with this formation type. The inclusion of flow results in spatial and temporal development of water chemistry and subsequently determines risks to water resources and human health. The main field injection and flow tank experiments in particular show leakage to develop according to several generalized phases of water chemistry. In the first phase of leakage a pulse of elevated major and minor ions coupled to moderate pH depression develops moving with flow. This behaviour is almost certainly a result of CO_2 induced rapid dissolution of reactive trace minerals (primarily amorphous and crystalline gibbsite at Vrøgum) combined with ion exchange. The main risks associated with this phase are attributed to the size of the aqueous ion peaks generated. For Vrøgum this involved mostly harmless species (i.e. Ca, Mg, Na, Si, Sr and Ba) and low peaks, thus risk was minimal. This may however be different in other silicate formations, depending on mineralogy and sediment properties. The second phase of leakage was manifest as decreasing aqueous ion concentrations coupled to increasing and persistent acidification. In this phase of leakage a zone of advanced acidification develops behind the pulse phase radiating out with flow. This increasing acidification appeared stepwise at Vrøgum and the work described in papers III and IV suggest this is likely the result of buffering exhaustion, i.e. depletion of reactive minerals (in this case gibbsite). The concept of buffering exhaustion suggests that for silicate aquifers like Vrøgum acidification increases with time. It suggests that during leakage pH may continually decrease towards a theoretical minimum, implying risks to water resources and human health may increase or at least change with maturity. For example, during the main experiment pH in the glacial sand adjacent to the injection plane initially decreased from 5.3 to approximately 4.9 whilst aqueous elements concentrations were elevated. By the end of the injection phase (i.e. after 72 days) pH had decreased to 4.4 and appeared to be still falling while aqueous concentrations had decreased. This theory is further supported by sediment alteration observed post injection inferring reactive minerals (i.e. buffering capacity) had been depleted (paper III). At lower pH's reached during this secondary phase other geochemical processes (i.e. further mineral dissolution, desorption and increased mobility of metal species) may now be induced which were not previously occurring at a significant rate. In Vrøgum this appears to manifest as increasing Al concentration, however in other formations additional toxic trace elements may potentially be mobilized inferring greater risk. Buffering exhaustion and increasing acidification need

not be a simple two step process as described here for Vrøgum. Presumably in a formation containing a variety of relatively reactive minerals a series of step wise increases in acidification could potentially occur, changing risk with time.

By employment of a 1 dimensional reactive transport model (paper IV) it was seen that (finite amorphous and crystalline) gibbsite derived Al^{3+} driven ion exchange could explain the majority of chemistry evolution observed in the field, including pulse phase and increasing acidification. Both amorphous and crystalline gibbsite dissolve under CO_2 induced acidified conditions thus:

$$Al(OH)_{3\ gibbsite} + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$$

Consequently increased Al^{3+} activity induces exchange processes, which in turn drives further dissolution of gibbsite generating the hydro-chemical evolution reported, e.g.

$$\frac{1}{3}Al^{3+} + \frac{1}{2}Ca - X_2 \leftrightarrow \frac{1}{3}Al - X_3 + \frac{1}{2}Ca^{2+}$$

Predictions for prolonged leakage (i.e. 3 years) made with the validated 1 dimensional reactive transport model show the pulse phase to travel through the aquifer with advective flow whilst the succeeding zone of advanced acidification grows indefinitely. This result suggests that large areas of an aquifer could potentially become significantly acidified with implications for risks posed to water resources. Other predictions showed risk increases with depth as higher P_{CO2} amplifies the processes observed. This infers the pulse phase would comprise higher peaks and sediment depletion may be more rapid leading to greater and faster acidification. Overall the work described highlights the complexity of assessing risk posed by sustained leakage of CO_2 from CCGS and introduces many novel concepts unique to this issue.

6.3 MMV program design

Informing design of efficient and accurate MMV programs is a key desired outcome of all shallow aquifer CO_2 contamination research, including the current thesis. The ultimate aim is to determine if and how CO_2 leakage from CCGS can be detected. Detection (i.e. detection of change in water chemistry as described in section 6.2) cannot be considered in a simplistic manner. Based on the work conducted in this thesis it is clear that during leakage water chemistry will evolve in time, space and with flow as well as vary between formation types. Consequently so will the most effective detection method. From this and other work it is clear that for carbonate dominated and mixed composition aquifers EC and carbonate related element increase (i.e. Ca and Mg) and pH decrease will imply leakage. Paper I in particular supports this however batch style experiments give little detail on how water chemistry will develop in time, space and with flow. Only the ZERT study currently provides information on in situ chemistry development in a carbonate dominated/mixed composition aquifer, however even this pioneering study is limited spatially and temporally. Consequently likely water chemistry development for such formations remains poorly understood.

This Ph.D. investigation has focused primarily on the effects of leakage on a silicate dominated shallow aquifers and consequently more insight has been gained relevant to MMV design in this formation type. Batch reactor studies conducted in paper I and technical report I concur with other published studies showing clearly pH and small elevations in certain dissolved ion concentrations will manifest during leakage into silicate dominated formations. However, these studies are arguably of low applicability as previously discussed, thus flow based studies conducted (i.e. tank and field experiments in papers II, III, IV and technical report II) provide the most valuable information on leakage evolution. These studies show that in a silicate dominated aquifer 2 (or more) distinct phases occur following continuous CO_2 contamination; a pulse phase succeeded by a zone(s) of advanced or increasing acidification. Geochemical signatures of these phases differ and consequently the most efficient method for detection will also differ depending on time and distance from the leak. This concept is demonstrated in Figure 21 which shows a theoretical silicate dominated shallow aquifer with CO_2 contamination originating from an abandoned deep borehole. During the early stages of contamination (Figure 21a) a pulse phase develops at the front of the dissolved CO_2 charged plume. The pulse phase, as described previously, is characterized by elevated major and minor ions (caused by mineral dissolution

driven ion exchange). This phase of leakage could be detected by EC, alkalinity and increase in some exchange based dissolved ions (which ions and by how much would depend on the formation).

Pulse phase groundwater pH will decrease however the degree to which is dependent on the amount of reactive buffering minerals present. In the flow based studies reported here for instance the reduction in pH during the pulse phase was around 0.3 – 0.6 units which may not be sufficient to conclude the cause is leakage alone (dependent on natural variation, as previously described [62]). The second phase involves depletion of reactive buffering minerals present and a reduced rate of dissolution driven ion exchange (based on the next reactive mineral present). This phase is characterized by decreases of elevated ions back towards natural levels (and therefore EC) coupled to further acidification (Figure 21b). This development was clear in both tank and field studies reported here where pH reduction increased to 0.9 – 1.6 units below background while aqueous ion concentrations dropped slightly. Efficient detection of leakage by water chemistry in this phase would depend on natural variation however would likely be by pH, EC, alkalinity and potentially dissolved element concentrations. The 3rd phase suggested here was not proven conclusively however inferred based on flow experiment observations (paper III and technical report II) and geochemical modelling (paper IV). First a secondary peak of dissolved elements forms at the interface of buffering exhaustion. This peak is caused by hydrodynamic dispersion and occurs where inflowing CO_2 charged groundwater travels through depleted aquifer sediment and reaches sediment with buffering capacity. Once acid groundwater encounters sediment containing gibbsite, dissolution is induced followed by ion exchange inducing a peak in dissolved elements. Up-gradient of this interface, maximal acidification has occurred. This phase conceptually represents total exhaustion of all buffering capacity during which aqueous ion concentrations return to practically background levels (and EC) while pH decreases further (Figure 21c).

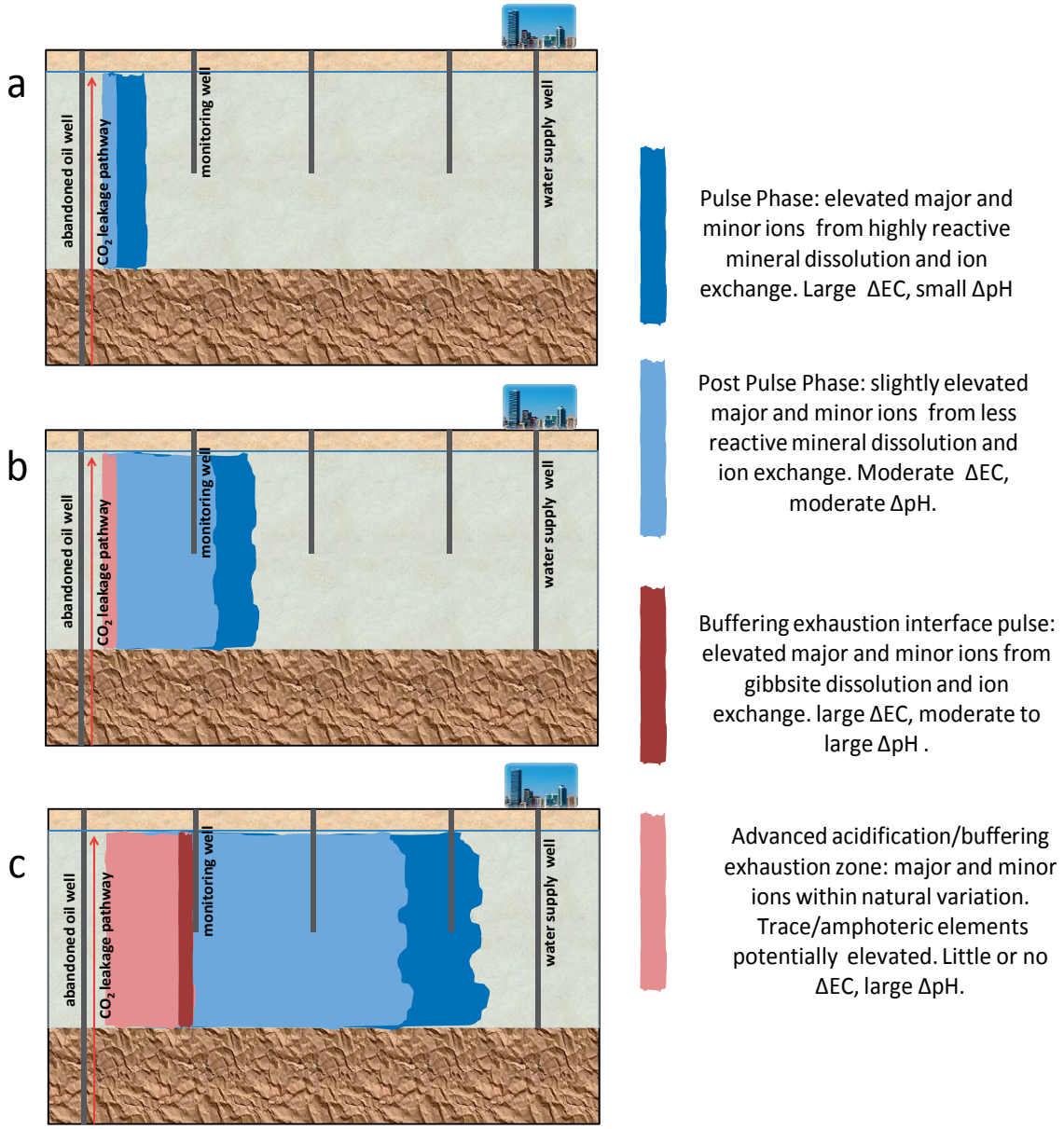

Figure 21. Theoretical silicate dominated aquifer showing development of chemistry in space at; a) early, b) intermediate and c) later times. Main phases of chemistry development identified during the pH study are shown demonstrating how risks to water resources and methods of most efficient detection may vary temporally and spatially.

In the flow based experiments buffering exhaustion was potentially observed in the later stages suggesting maximum acidification was being approached. From the geochemical modelling it was seen that finite amounts of a buffering mineral were required to simulate most accurately the observed water chemistry evolution, more specifically small amounts of reactive (amorphous) and less reactive (crystalline) gibbsite. In the model presented in pa-

per IV once these finite amounts of minerals are consumed during buffering a zone of advanced acidification is formed radiating out from the leak. The experimental observations and validated model created during this Ph.D. support this theory of buffering exhaustion which would be the ultimate phase of leakage in a silicate dominated aquifer representing the time when only relatively un-reactive minerals remain (e.g. quartz and feldspars). This zone would be best detected by alkalinity and pH decrease which would now be significant and approach the theoretical minimum based on the P_{CO2} achieved (in this case 4.1). In this zone EC and aqueous ion concentration may now be within natural variation and thus not provide conclusive evidence of a leak. Although a site specific study this distinct chemistry evolution appears fundamental and should be relatively applicable to other similar silicate dominated aquifers.

7 Conclusions

Based on the work presented in this thesis the following general conclusions can be drawn regarding the risks attributable to CO_2 contamination in shallow potable aquifer systems:

- The method of investigation used will influence results and thus applicability should be understood before conclusions are drawn.
- The studies presented infer batch reactors may indicate a "worst case" scenario for pH and some dissolved elements. However although relatively comparable to flow/field methods, spatial and temporal detail is lost. Furthermore, use of groundwater (as opposed to de-ionized water) gave results more comparable to field/flow methods.
- Risks to water resources will be site specific however can be generalized by aquifer type:
    - Carbonate dominated aquifers (>2%TIC) will exhibit severe increases in aqueous element concentrations with moderate to low levels of acidification due to carbonate mineral buffering. Risks are inferred by high levels of carbonate related elements and their substituting cations, which in general are not significantly toxic, however may pose operational issues.
    - Silicate dominated aquifers (<2%TIC) will exhibit small to moderate increases in aqueous element concentrations and significant acidification caused by low levels of reactive mineral buffering coupled to ion exchange. Risks are inferred by mobilization of amphoteric pH sensitive trace elements once advanced acidification is achieved.
    - Mixed sediment formations will exhibit severe increases in aqueous ion concentrations including increases in many potentially toxic trace metals and moderate acidification. This is caused by carbonate, clay and reactive silicate mineral buffering and significant exchange/surface processes. Subsequently risks are inferred by high levels of major and trace elements.
- Reactivity of host minerals is a major control on risk posed by leakage with actual elemental abundance within sediment less important.

- Relatively low carbonate composition can provide a large buffering capacity (i.e. inferred as >2% TIC) reducing susceptibility to acidification significantly influencing risks to water resources.
- Low carbonate content (i.e. inferred as <2% TIC) infers high susceptibility to acidification influencing risks to water resources.

Based on the work presented in this Ph.D. thesis the following conclusions can be drawn regarding the risks attributable to CO_2 contamination in silicate dominated shallow aquifer systems such as Vrøgum:

- The effects of flow are paramount; creating distinct temporal and spatial water chemistry evolution. Consequently risks posed to water resources vary in time and space.
- A rapidly developing advective pulse like phase, characterized by elevated aqueous ion concentrations and EC, is a key geochemical signature of leakage. This behavior is caused by flow and rapid dissolution of reactive trace minerals inducing ion exchange and surface processes.
- Buffering in silicate dominated aquifers such as Vrøgum is initially provided by small finite amounts of reactive trace minerals which are depleted and flushed. Following depletion, buffering capacity is exhausted thus increased acidification is observed. This water chemistry evolution infers risks change with time and pH dependent amphoteric elements may be mobilized as a leak matures.
- Decreased dissolution observed during buffering depletion reduces ion exchange thus pulse phase aqueous ion concentrations decrease towards background. Consequently they may be poor indicators for leakage at this stage.
- Gibbsite derived Al^{3+} driven cation exchange most likely controls the majority of water chemistry change at Vrøgum with Al concentrations seen to be the most significant threat to water resources. This will likely be applicable to other similar sites.
- The behavior of some aqueous element concentrations is poorly understood, in particular Fe and Mn, for which decrease to zero concentration was observed. Results suggest this is most likely caused by some form of precipitation; however the precipitate or mechanism was not

identified in the current study. The processes controlling these elements aqueous concentration require further study.

- Sediment alteration was observed following sustained CO_2 contamination including changes in exchange composition and depletion of reactive mineral species. Results support suggested mechanisms of water chemistry change, i.e. buffering exhaustion. This phenomenon will likely be applicable to other similar formations.
- Following buffering depletion, numerical modeling suggests sustained leakage would result in a growing area of advanced acidification potentially forming a significant risk to water resources.
- Numerical modeling suggests buffering depletion is more rapid with depth and thus water chemistry change more severe therefore increasing risks to water resources.
- The most effective method of leak detection will vary between formations, spatially, temporally and with flow. Thus an integrated site specific approach should be developed based on the principles highlighted in this study.

8 Future perspectives

The effects of sustained in situ leakage over significant temporal and spatial scales in all aquifer types (i.e. carbonate dominated and mixed) need to be further characterized. In particular the phenomenon of buffering exhaustion and increasing acidification needs to be understood if risks posed to water resources are to be assessed and efficient MMV programs designed.

The work conducted here on a silicate dominated aquifer shows clearly the importance of consideration of flow on water chemistry evolution and consequently risks to water resources and leakage detection. Based on results reported here it is logical to assume formations of a different composition (i.e. carbonate dominated) will exhibit distinct water chemistry evolution with flow, perhaps in a related manner, however this is currently unknown.

Greater temporal and spatial scales more relevant to leakage should also be studied in order to prove more conclusively the longer term effects, some of which have been suggested here.

Concentration development of some aqueous elements is poorly understood (i.e. Fe and Mn). Consequently they need to be studied in more detail to identify and quantify controlling processes.

Further geochemical modelling studies should be conducted using validated models (such as reported here) to further quantify and understand controlling factors and mechanisms and make more general conclusions regarding risks and detection.

Effects of leakage on sediment composition of all types (i.e. silicate dominated, carbonate dominated and mixed) should be further investigated. Whilst alteration of sediment at Vrøgum seemed conclusive (paper III), the ZERT core studies (technical report III) demonstrated this phenomenon is poorly understood and requires further study.

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Papers and Technical Reports

Papers

I Cahill, A.G., Jakobsen, R., Mathiesen T.B., Jensen, C.K. Risks Attributable to Water Quality Changes in Shallow Potable Aquifers from Geological Carbon Sequestration Leakage into Sediments of Variable Carbonate Content. Accepted for Publication: International Journal of Greenhouse Gas Control.

II Cahill, A.G., Jakobsen, R., Hydro-geochemical impact of CO_2 leakage from geological storage on shallow potable aquifers: A field scale pilot experiment. In Press: Int. J. Greenhouse Gas Control (2013), http://dx.doi.org/10.1016/j.ijggc.2013.03.015 -0.

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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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